THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. LII NOVEMBER 1957 No. 11

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

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VEGETABLE TANNING MATERIALS

Consistent High Tannin... Consistent Color... Consistent Quality

Whatever your requirements, for VEGETABLE TANNING MATERIALS you can put your confidence in us as your prime and continuous source of supply. Prompt shipments.

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LII NOVEMBER 1957 No. 11

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Cover—The Eastern Regional Research Laboratory located at Wyndmoor, Pennsylvania, one of the laboratories of the Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

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POWDERED SUPER SPRUCE

LACTANX

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Robeson Process Company

General Offices and Plant
ERIE, PA.

There's More-Much More

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Extracts and Raw Tanning Materials
From the Most Complete Line of Brands

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Ordinary	Clarified
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Myrabolams, Divi-Divi, Mangrove, Valonia, Sumac and Other Vegetable Tanning Materials from All Parts of the World.

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To prevent SPOILAGE

USE.. BSM-11

as part of Good housekeeping practice

BSM-11 is highly effective in controlling the growth of microorganisms which digest hide substance during processing. BSM-11 is a liquid, thus easily added to the systems directly from the drums.

It has been demonstrated in many tanneries that the synergistic combination of bactericides and fungicides in BSM-11 provides efficient, economical control of bacteria, molds and yeasts which damage skins and hides.

Our representative will give technical assistance on the most effective use of BSM-11 in your process.

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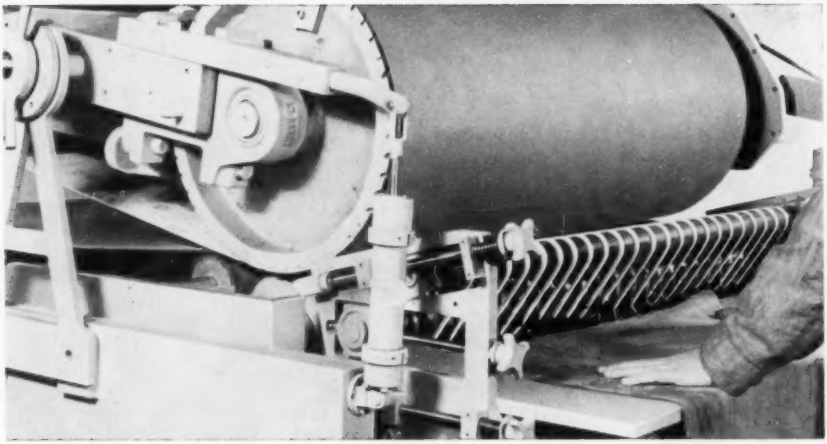
Manufacturing Chemists • Memphis 8, Tennessee • Representatives in Most Countries

MICROORGANISM CONTROL SPECIALISTS



LEATHER BUFFING PRODUCTION TRIPLED...

with new "Speedbuffer" and 3M Abrasive Belts.

With production increases of 330% in leather buffing . . . the "Speedbuffer" is the first machine to use 3M Coated Abrasive Belts for leather sanding. Abrasive Belts contain up to three times more abrasive surface than conventional buffing abrasives—can be run 20% faster—are cooler running — produce consistently superior results. Belts last far longer, too, and are easier to change—thus cutting down-time.

The new "Speedbuffer" also permits automatic straight line conveyorizing to a brusher, a second sander, or a stacking machine. Handling costs are cut drastically because the leather is sanded on top, and hides do not have to be turned over to be cleaned..

Ask your 3M Representative for a **FREE** showing of the new motion picture on belt sanding in the leather industry. He can give you full information on cost-cutting 3M Abrasive applications for your plant, too. For a complete line of coated abrasives for all leather applications, always look to 3M first.

3M ABRASIVES

*"Speedbuffer" is a trade name of Timesaver, Inc., Robbinsdale, Minn.

3M Coated Abrasives are made in U.S.A. by Minnesota Mining and Mfg. Co. General Offices: St. Paul 6, Minn. In Canada: P. O. Box 757, London, Ontario. Export Sales Office: 99 Park Avenue, New York City.

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ARKO®
FAT LIQUORS
for finer leathers

ARKO BASE C

a superior suede oil—
produces soft, mellow
leather with a tight, round
feel, and well nourished nap
without excess sheen; does
not mark up when rubbed

ARKO FAT LIQUOR G P S

gives a tight, soft feel to white or light colored leathers—garment sheep or side leathers; soft shoe uppers and chrome linings

ARKO FAT LIQUOR L C

for a light, fluffy feel on white or light colored
glove, garment and soft shoe leathers
blend with Arko Fat Liquor GPS to produce
soft, clean leathers with tight, fine break

ARKO FAT LIQUOR L M

for colored cow, horse, sheep shoe or garment leathers
rich blend of marine and cocoanut oils with added moellon
excellent topping oil for rich colors

ARKO FAT LIQUOR M C A

fine topping for white or light colored leathers
excellent for shearlings
a white stable nonionic emulsion of marine and
neatsfoot oils; applied in the drum or tan paddle

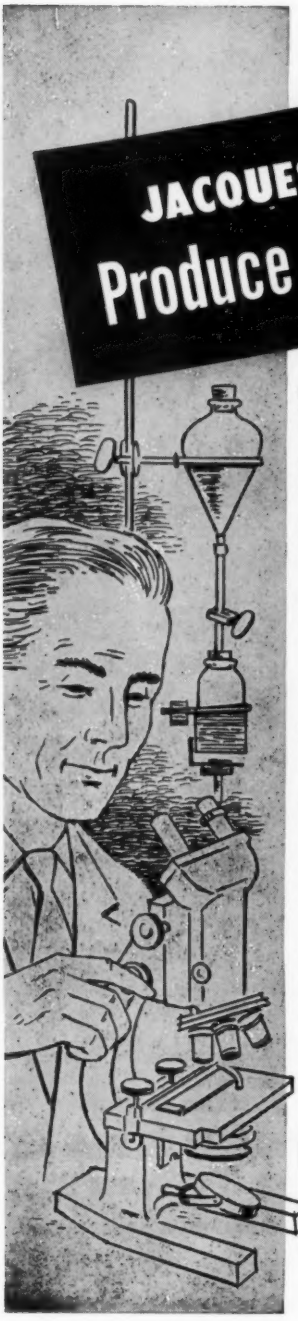
● **WRITE FOR TECHNICAL SERVICE BULLETIN.**

ARKANSAS CO., INC.

serving the tanning industry for over 50 years

NEWARK • NEW JERSEY

AC INC.



JACQUES WOLF CHEMICALS Produce High Grade Leather

SYNEKTAN 0-230*—For use alone or in combination tanning with vegetable extract or chrome. Useful for rapid tannages and bleaches. Excellent as a retan on chrome stock.

SYNEKTAN 0-272*—Similar to Synektan 0-230 in use. Produces smooth grain leather with mellow feel.

SYNEKTAN NPP*—For high grade white leather of improved light-fastness. Also used in combination with Alum, Chrome, and in producing pastel shades. Produces full, soft leather of good weight.

SYNEKTAN NCRP*—Recommended for Sport goods, Suede and Elk leathers. Produces full, plump, fine grained leather, of good tensile strength.

FAT LIQUORS—For all types of leather. Special quality fat liquors with high lubricant effects and excellent light fastness for whites.

TANASOL PW*—Syntan in beads, to use with Tanasol NCO for bleaching chrome stock and in retanning chrome stock. In the dye bath for good level colors.

TANASOL NCO*—Syntan in beads, to use with extracts in the tanning and retanning operations.

FUNGIZYME* BATES—Pancreatic bating salts of standard, controlled quality.

BATE A & AS—For sheep skins and sole leather.

BATE B & BS—For furniture leather, side leather and calf skins.

SULPHONATED OILS—(Various Bases.)

MONOPOLE OIL*—(For Finishing.)

EMULSIFIERS AND DETERGENTS—For good degreasing.

Samples and information upon request.

JACQUES WOLF & CO.
Chemicals PASSAIC, N.J.

***Plants in:* Clifton, N.J., Carlstadt, N.J., Los Angeles, Calif.**

* Reg. U. S. Pat Office.

New tanning-mates

give plumper, tighter, brighter

WHITE LEATHER

ZIRCOTAN S / LEUKANOL C

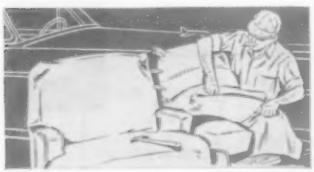
TWO NEW LEATHER CHEMICALS RECENTLY DEVELOPED BY ROHM & HAAS

These white leather samples are being subjected to hundreds of thousands of flexings from pounding weights in a grueling flex test at the Rohm & Haas Leather Research Laboratories.

Now you can get a plumper, tighter, brighter white leather by using ZIRCOTAN S and LEUKANOL C in your tanning formulation. This new tanning combination fills the hide thoroughly, and gives the finished product that *luxury feel* so characteristic of fine upholstery leather.

Leathers tanned with ZIRCOTAN S and LEUKANOL C also develop better temper, tighter break, and brighter whites. They're tough and resilient and will take lots of wear and flexing. The white extends all the way through the leather and is virtually light fast. The white *stays* white!

You'll want to know more about our new tanning-mates, ZIRCOTAN S and LEUKANOL C . . . and our many other leather chemicals and services.



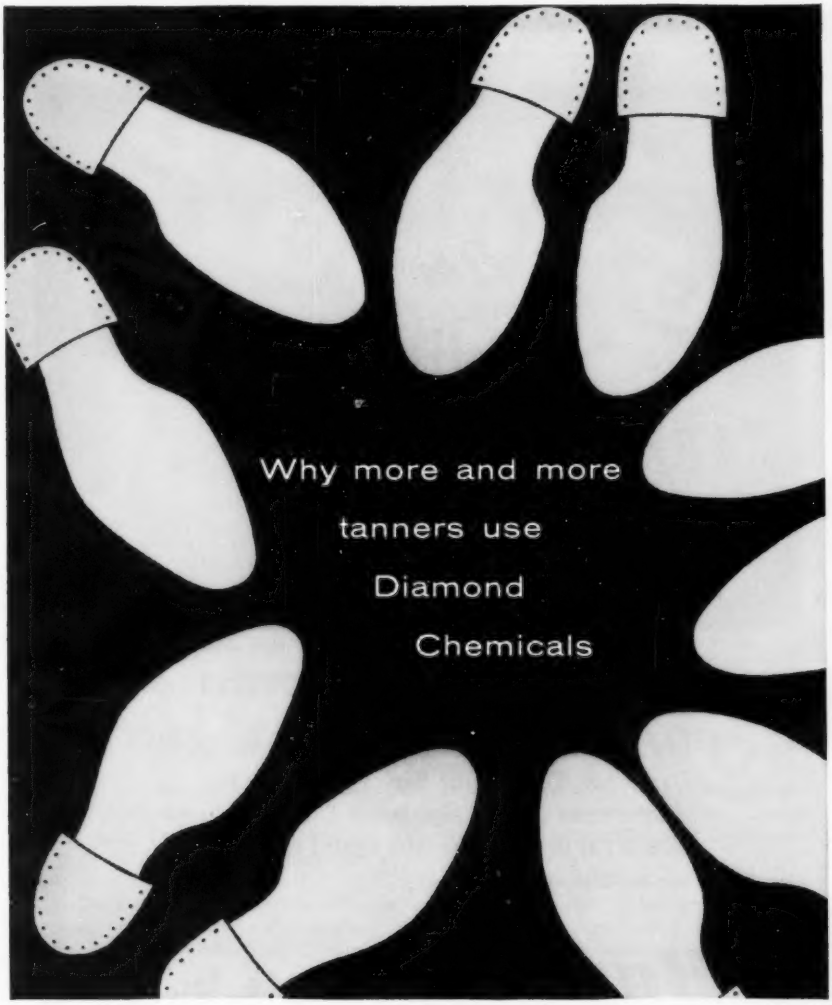
ZIRCOTAN *and* LEUKANOL *are trade-marks, Reg. U.S. Pat. Off. and in principal foreign countries.*

Chemicals for Industry

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

Representatives in principal foreign countries



Top-notch tanners learned long ago that high quality leather comes from uniform process control and the finest tanning materials.

To these tanners, DIAMOND means consistently dependable, always uniform chemicals—Tanolin®, bichromate, fat liquors or neutralizers. The reason why lies in DIAMOND's processing control at every step from raw material to shipped product.

Fast delivery from eight strategically located warehouses pleases most tanners, too. Call your nearby DIAMOND representative for information. He's trained in leather chemistry and backed up by DIAMOND's entire technical staff. DIAMOND ALKALI COMPANY, 300 Union Commerce Building, Cleveland 14, Ohio.

Diamond Chemicals

Mellow Leather...

The present day demand for mellow leather is best met by incorporating 10 to 15% of Myrabolams in the blend.

Myrabolam Extract is the most mellow of all the tanning materials in popular use today and its consumption in this country has shown a striking increase in the last three years.

In Calder & Mersey Extract Co.'s spray dried Myrabolam Powder, the Barkey Importing Co. has the finest colored Myrabolam Extract available. It has been magnetically treated to remove all metallic impurities.

Barkey Importing Co., Inc.

44 EAST 53RD STREET • NEW YORK 22, N. Y.

Save time handling sulfides in new fast-pouring drum

You'll like the time you'll save with this new 400-lb. drum in which you can now purchase Hooker sodium sulfide and sodium sulfhydrate. Your operators will like its convenience, too.

The opening is 18 inches in diameter—four inches wider and 65% larger in area than the former container.

Easier, quicker to empty

This drum is much easier to empty with a scoop or shovel. It saves time when pouring, too. Flakes don't pile up around the opening when the drum is inverted.

You'll also like the way this drum safeguards the exceptionally low iron content of our sulfide or sulfhydrate until you're ready to use it.

Only brand-new drums are shipped; none are re-used. A lacquer lining prevents iron pickup during shipping and storage. Six lugs hold the lid on tight and let you reseal the drum to protect any unused product.

There's no increase in price for the new drum. To get this extra convenience, just specify *Hooker* sodium sulfide or sodium sulfhydrate on your next order.

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For low-cost, latex-pigment finishing try...

Naugatuck's Nitrex

Get the *color* that Fashion now demands in leather, with this economical *latex-pigment binder.* It's your low-cost way to obtain a high-style, oil-resistant, scuff-resistant finish...a finish that embosses beautifully!

NITREX® is a non-flammable, colloidal, aqueous dispersion of a nitrile-type synthetic rubber noted for its ability to resist the effects of organic solvents, such as fats and petroleum oils and solvents. Also, the particle size and the specially-developed emulsifier system used in this latex compound make it particularly suitable for impregnation of the leather's surface. When dried, its film is translucent, permitting the true color of the pigment to come through.

For all your latex needs, and for reliable application assistance, think first of Naugatuck, world's leader in latex production and compounding.

United States Rubber

Naugatuck Chemical Division

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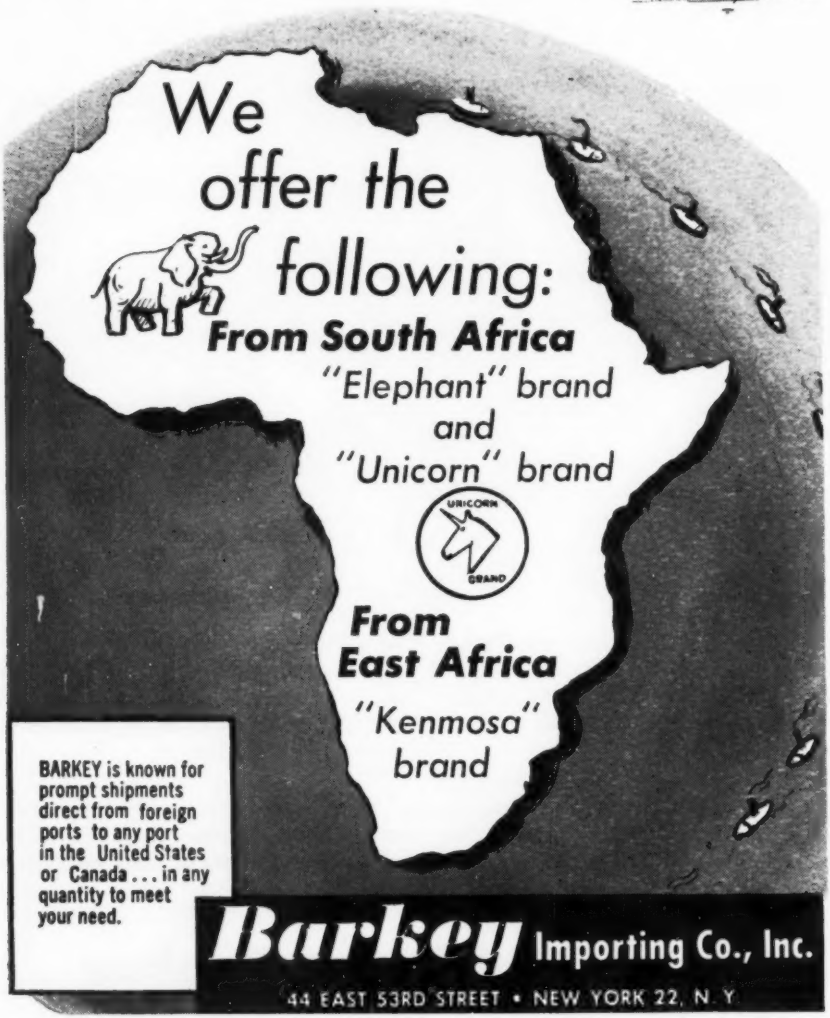
is headquarters for

WATTLE EXTRACTS


We offer the following:
From South Africa
"Elephant" brand
and
"Unicorn" brand
UNICORN
BRAND
From East Africa
"Kenmosa" brand
BARKEY is known for prompt shipments direct from foreign ports to any port in the United States or Canada . . . in any quantity to meet your need.
Barkey Importing Co., Inc.
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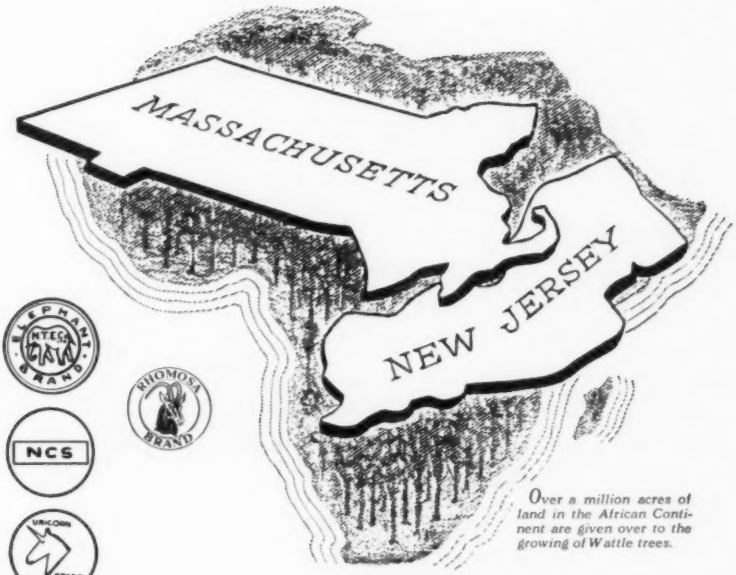
WATTLE...a million acre crop



Over a million acres of land in the African Continent are given over to the growing of Wattle trees.

How big is 1,000,000 acres? It's more than the combined areas of two states prominently identified with leather production . . . Massachusetts and New Jersey.

Imagine these two states entirely covered with scientifically-cultivated forests of the Wattle trees! That gives you an idea of the extent of this crop and its dependability for the needs of tanners throughout the world.

Wattle is a pure extract, untreated in any way by chemicals. It keeps the salts content of tanning liquors down to a minimum. Clear solutions, regardless of pH, with least sludge deposits, are the inevitable result.

WATTLE MAKES GOOD LEATHER

KENMOSA EXTRACT

SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO.
Pietermaritzburg, Natal, Union of South Africa

KENYA WATTLE MANUFACTURERS ASSOCIATION
Nairobi, Kenya, East Africa

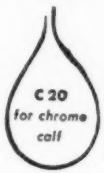
famous

TANNERY

"HOUSEHOLD NAMES"

Every industry has its famous names. In tanning, Atlas, and the products it has developed through the years, all are "household names"—respected because they represent the finest of their kind and for their purposes.

How many of those names do you recognize as "old friends?" How many of the new ones are you familiar with?



Atlas, keeping apace of, and frequently leading the way to, new progress in tanning, brings you the products best suited to your needs.

It is a fact that when tanners change to Atlas Fatliquors, few ever change again.

Atlas **REFINERY, INC.**
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NEWARK 5, N. J.

Emulsifiers

for the Leather Industry for Hide Degreasing Chrome Tanning Fatliquoring

Antaron® FC-34

Emulphor® EL-620, EL-719, ON-870, VN-430

Emulphogene® AM-870

Igepal® CO-530, CO-630, DM-710

Katapol® PN-430

Antara offers to the leather industry a wide range of anionic, nonionic and cationic surfactants to emulsify various oils, fats, and waxes.

TYPICAL APPLICATIONS INCLUDE:

PICKLE DEGREASING OF HIDES
—to provide a powerful emulsifying action;

CHROME TANNING
—to promote uniform takeup of chrome, thereby overcoming subsequent "window framing";

FATLIQUORING
—to control the stability, softening effect, lubrication, and penetrating characteristics of fatliquor formulations.

KATAPOL PN-430

is a new cationic emulsifier which provides maximum retention properties to fatliquors; it is soluble in a variety of animal, vegetable, and mineral oils.

For full information on the Antara emulsifier that will do the best job for you, call or write our nearest branch office.

From Research to Reality

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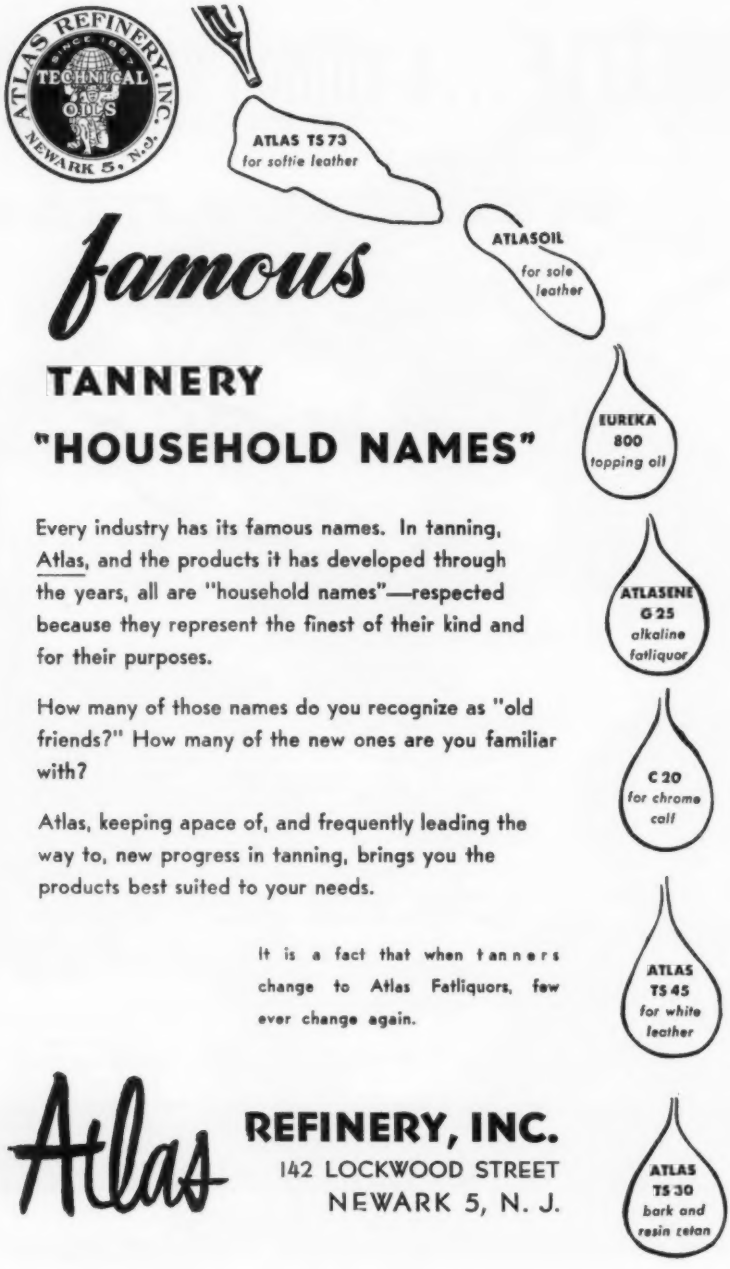
SALES OFFICES: New York • Boston • Providence • Philadelphia • Charlotte • Chattanooga • Chicago • Portland, Ore. • San Francisco • Los Angeles. IN CANADA: Chemical Developments of Canada, Ltd., Montreal



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88 YEARS
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The J. S. Young Co., importers, manufacturers and processors, is in a position to supply tanners with practically every known reputable dyewood and tanning extract—from every part of the world.

Deliveries are made as ordered, when ordered—in any quantity from a barrel to a tank car or tank truck. Shipments can be made direct from Baltimore, or from our warehouses in Peabody, Mass., or Chicago.

The J. S. Young Co. is your stable, dependable, source of supply.

Manufacturers of the famous Chembark Natural tanning extracts for the Chemtan Co. and other special products.

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WATTLE BARK
FROM EAST AND SOUTH AFRICA
GAMBIER
FROM MALAYAN STRAITS
MYRABOLAM
FROM INDIA
QUERBRACHO
FROM THE ARGENTINE
CHESTNUTWOOD EXTRACT
FROM FRANCE AND ITALY
SUMAC
FROM SICILY
DIVI-DIVI
FROM SANTA DOMINGO
HEMLOCK
FROM ASIA
FUSTIC DYEWOOD
FROM CENTRAL AMERICA
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FROM NICARAGUA
OSAGE ORANGE
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FROM HAITI
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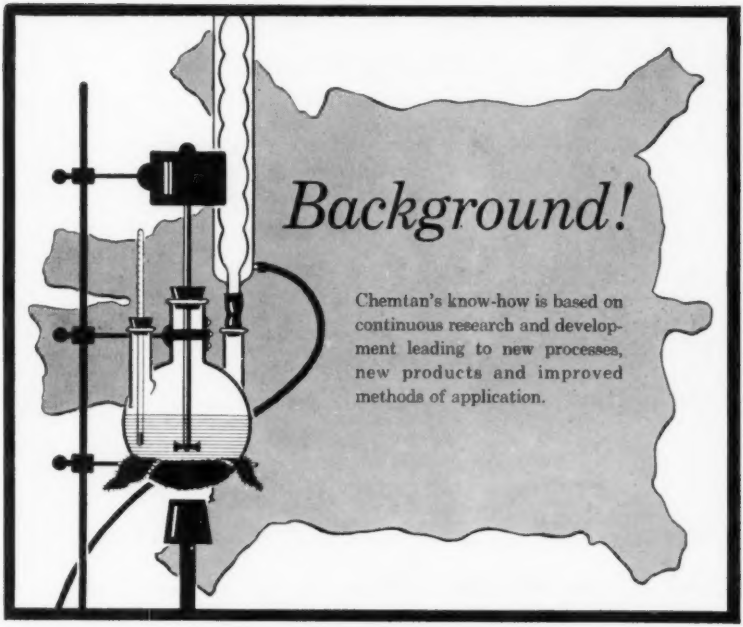

Background!
Chemtan's know-how is based on continuous research and development leading to new processes, new products and improved methods of application.

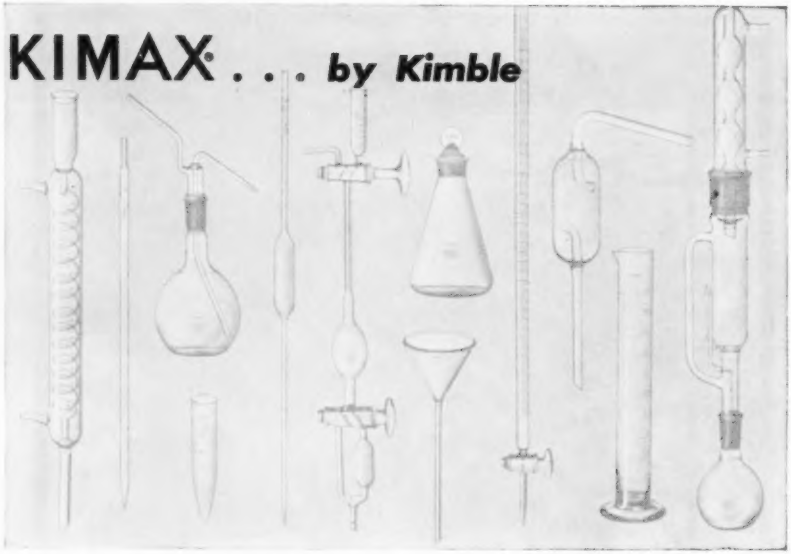
CHEMTAN R-4 and R-6

Chemtan R-4 and R-6 represent a group of resins which have gained world-wide recognition within a few years. They are high polymers, yet water soluble and will penetrate untanned or tanned hides. Their high filling value and other properties mean making better leather from inferior hides.

There are unlimited possibilities of creating new types of leather or modifying established procedures. Chemtan R-4 and R-6 may be applied on chrome tanned leathers or be used at any other stage and combined with all known tanning agents. One of Chemtan's Tannery and Laboratory Trained Men will be glad to demonstrate these products.

CHEMTAN COMPANY
EXETER, NEW HAMPSHIRE

All our facilities are devoted exclusively to the tanning industry



KIMAX . . . a new line of borosilicate laboratory glassware

KIMAX . . . trademark for a hard borosilicate glass now being made by the Kimble Glass Company under the designation KG-33. Available in a line of laboratory shapes and sizes, both graduated and chemical ware, which embodies the well-known Kimble quality, craftsmanship and accuracy.

KIMAX borosilicate glassware offers the following:

- **High resistance to heat, mechanical shock and chemical attack.**
- **Low coefficient of expansion. Easily worked and sealed to borosilicate glass of similar properties.**
- **Graduated ware individually retested to insure accuracy.**
- **Can be combined with standard flint glassware to qualify for quantity discounts.**

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COLLAGEN REACTIVITY WITH METALS*†

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INTRODUCTION

The reactivity of collagen with metals has many important aspects, two of which will be considered in this paper. Collagen, as the most prevalent organic constituent of skeletal tissue, undoubtedly plays a role in the binding of those metal elements which, when introduced into vertebrate animals, are known to become associated with the organic complex of bone. The radioactive metal plutonium is such an element (1). Other metallic elements such as strontium and lead, known to become associated with the inorganic complex of skeletal tissue, should not react with collagen. Therefore, demonstration that collagen *in vitro* reacts with certain metals and not with others will provide useful information for the design and execution of *in vivo* experiments to establish therapeutic measures for removal of toxic metals from skeletal tissues of living organisms.

The second aspect of this subject concerns leather manufacture. A major proportion of leather manufactured today is nothing more than chrome-tanned collagen. Even though during the past seventy-five years there have been numerous investigations on the chrome tanning process, the mechanisms involved are not completely understood. The observations and data to be presented in this paper suggest a possibility for one mechanism involved in chrome tanning. Using this mechanism as a basis, it should be possible to find compounds containing metals other than chromium as mineral tanning agents.

Much information concerning the reactivity of collagen with metals may be obtained from electronoscopic observations and shrinkage temperature (Ts) measurements before and after treatment of the protein with compounds containing metals of specific interest. Combination of collagen with metals increases the electron density of the protein; therefore, electron images of collagen-metal compounds will have greater contrast than electron images of collagen alone. This phenomenon is termed electron staining. Thus, electronoscopic appearance becomes a criterion for the combination of collagen with metals. The shrinkage temperature of collagen is an index of the number and strength of the cohesive forces holding the collagen molecules to-

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gether as fundamental structural units or fibrils. A lowering of the Ts as a result of metal compound treatment indicates the rupture of cohesive forces; a raising of Ts as a result of metal compound treatment indicates an increase in the number of intermolecular bonds in the fibrils; no change in Ts indicates noninvolvement of the crosslinks of collagen fibrils. Thus, shrinkage temperature becomes another criterion for the evaluation of the reactivity of collagen with metals.

The purpose of this paper is to present electronoscopic observations and shrinkage temperature data on collagen treated with metallic compounds which on dissociation yield metal or metal-containing ions which have properties governing their (metals) reactivity with collagen.

EXPERIMENTAL

The collagen used in this work was obtained from air-dried, purified, cowhide corium cubes. The cubes were comminuted in a blender, and the fibrils were isolated by repeated centrifugation and washing. The dispersions contained from 0.05 - 0.10 mg. collagen per ml. The reagents, the metals of interest, their atomic numbers, and the hydrogen ion concentration of the reagent solutions are listed in Table I. Unless otherwise noted, the reagent solutions were made up on a 1%, weight/volume basis.

Reaction mixtures were prepared by adding one volume (usually 1 ml.) reagent solution to nine volumes (9 ml.) of collagen dispersion, mixing thoroughly, and allowing the mixture to stand at room temperature for at least 15 minutes before further processing. It was found that 15 minutes was more than sufficient time for the reaction of collagen with any of the reagents listed

TABLE I

Reagent	Metal of Interest	Atomic Number	pH of Reagent Solution
Chrome alum*	Cr	24	2.8
Strontium choride	Sr	38	5.9
Silver nitrate	Ag	47	6.2
Barium chloride*	Ba	56	5.7
Phosphotungstic acid	W	74	2.0
Sodium tungstate	W	74	9.0
Osmium tetraoxide	Os	76	4.6
Mercuric chloride	Hg	80	3.5
Lead acetate	Pb	82	6.2
Lead nitrate	Pb	82	4.5
Uranyl acetate	U	92	4.5
Uranyl nitrate	U	92	2.8
Plutonium nitrate*	Pu	94	1.0

*Chrome alum, 3%; barium chloride, both 1% and 10%; plutonium nitrate, 0.1% plutonium metal in 1 *N* HNO_3; all others 1%.

in Table I. The pH of the reaction mixture was determined, and a sample was withdrawn for electron microscopy. A second fraction of the reaction mixture was then washed with distilled water by repeated centrifugations or dialyses, and a sample was again withdrawn for electron microscopy. The remainder of the washed reaction mixture was used for shrinkage temperature determinations by the microscopic shrinkage temperature method (2).

Specimens were prepared for electron microscopy by placing small droplets of the reaction mixture on collodion-covered specimen-supporting screens and allowing them to dry in air before examination in the electron microscope. Representative fields were usually photographed at magnifications of 6,500 or 10,000 diameters. The electron micrographs used to illustrate this paper are photographic enlargements.

RESULTS AND DISCUSSION

A description of untreated collagen serves as the basis for comparison with the treated collagens. Collagen fibrils, Figure 1, are indefinitely long compared with their width of about 0.1 micron. They are banded transverse to their long axis, forming macroperiods which average 650 A. in length. Close inspection of the dark bands, Figure 1a, reveals that they consist of two or more components. Intraperiod components are more clearly defined in the shadowed preparation, Figure 1b. It is believed that the dark bands (raised portions in the shadowed preparation) correspond to loci of high basic amino acid content, and that the light bands (depressed portions in the shadowed preparation) represent loci of high water content of collagen fibrils in their natural state. Contrast is low in Figure 1a because there is little difference between the electron density of the collagen fibrils and that of the collodion-supporting film. The good contrast in Figure 1b is a result of the deposition of an electron-dense material (in this case, tungsten oxide) at an angle onto the surface of the specimen. This technique for enhancing contrast is termed shadow-casting (3). It is a physical method and has no significance as a criterion for evaluating collagen reactivity with metals.

The reagents listed in Table I may be separated into two categories: those which affect the collagen fibrils by increasing their electron density, termed "electron stains", and those compounds which have no effect on the electron density of the fibrils. The latter group of reagents, termed "nonreactive" compounds, will be considered first. Table II summarizes the data on the treatment of collagen with nonreactive compounds.

The data in Table II demonstrate the following: in all instances, excepting the sodium tungstate, the metal of interest is a cation or part of a cationic complex; the pH values of the reaction mixtures are between the pH of the collagen dispersion and the pH of the particular reagent solution; the collagen from the washed reaction mixtures was not electron-stained; the shrinkage temperatures of the collagen from washed reaction mixtures generally were

not affected or were lowered by the treatment; and where the shrinkage temperatures were lowered appreciably, the collagen fibrils were swollen to a marked degree.

For all practical purposes, collagen in media having pH values between 5.0 and 8.0 is essentially neutral. Within this pH range neutral collagen will neither attract nor repulse metal or metal-containing ions regardless of charge. The net positive charge on collagen increases as the hydrogen ion concentration increases; thus if the medium has a pH of less than 5.0, the positively charged collagen will repulse the metal or metal-containing cations. This is borne out by the electronoscopic observations.

From the descriptions in Table II it is noted that if the collagen sample was taken from unwashed reaction mixtures, the presence of reagent could always be detected in the form of crystals, opaque (electron-dense) films, or

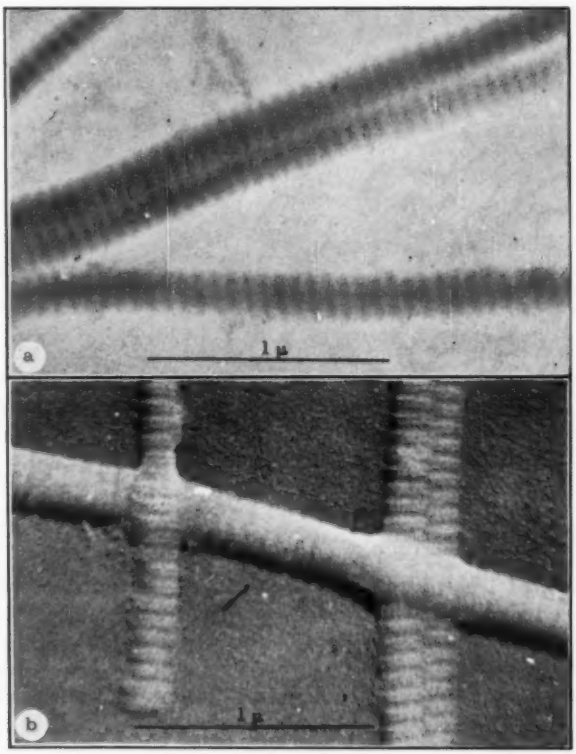

FIGURE 1.—Collagen Fibrils from Control Dispersion. 37,500 ×.
a. Note the low electron density or contrast. Macroperiod=650 A. (avg.).
b. Fibrils shadowed with tungsten oxide and carbon. Each macroperiod consists of two raised intraperiod bands.

TABLE II

SUMMARY OF DATA ON TREATMENTS WITH "NONREACTIVE" COMPOUNDS

Treatment	Ionic State of Metal	pH: Reagent Solution	pH: Reaction Mixture	Electron Staining*	Ts °C.†	Remarks‡
None (control)	—	—	6.0	—	63	Cf. Figure 1.
Strontium chloride $SrCl_2$(**)	Sr^{++} (38)††	5.9	6.0	None	59	Salts precipitated out over surface and along edges of fibrils. Fibrils slighty swollen.
Silver nitrate $AgNO_3$	Ag^+ (47)	6.2	6.0	None	63	Silver particles precipitated along edges and on surface of fibrils.
Barium chloride $BaCl_2$	Ba^{++} (56)	5.7	6.0	None	63	Barium salts precipitated along edges and on surface of fibrils. Fibrils treated with 10% $BaCl_2$ solution, swollen at irregular intervals along fibril length.
Sodium tungstate Na_2WO_4	WO_4^{--} (74)	9.0	6.0	None	63	Tungsten precipitated out as film (continuous and discontinuous) on surface and along edges of fibrils.
Mercuric chloride $HgCl_2$	Hg^{++} (80)	3.5	4.2	None	63	Salts precipitated out on surface and along edges of fibrils.
Lead acetate $Pb(C_2H_3O_2)_2$	Pb^{++} (82)	6.2	6.0	None	60	Salts and lead particles precipitated out over surface and along edges of fibrils.
Lead nitrate $Pb(NO_3)_2$	Pb^{++} (82)	4.5	5.3	None	46	Cf. Figures 2 and 3.
Uranyl nitrate $UO_2(NO_3)_2$	UO_2^{++} (92)	2.8	3.8	None	43	Fibrils swollen; salts and particles precipitated out over surface and along edges of fibrils.

*Electron staining refers to an increase in electron density of fibrils obtained from washed reaction mixtures.
†Ts = shrinkage temperature of collagen from washed reaction mixtures.
‡Remarks = electronoscopic appearance of collagen from reaction mixtures before washing.
**Water of hydration excluded from formulae.
††Numbers in parentheses are the atomic numbers of the metals of interest.

metal particles. These often obscured the collagen fibrils to the point where macroperiodicity or intraperiod bands could not be determined. No evidence of metal could be found in the electron micrographs of collagen fibrils from washed reaction mixtures, with the exception of occasional particles enmeshed in fibril nets. The swelling noted for fibrils treated with strontium chloride, barium chloride, lead acetate, lead nitrate, and uranyl nitrate is ascribed to the fact that Sr^{++}, Ba^{++}, Pb^{++}, and UO_2^{++} are lyotropic cations.

The electron micrographs (Figures 2 and 3), of lead nitrate–treated collagen from unwashed reaction mixtures are of particular interest because they il-

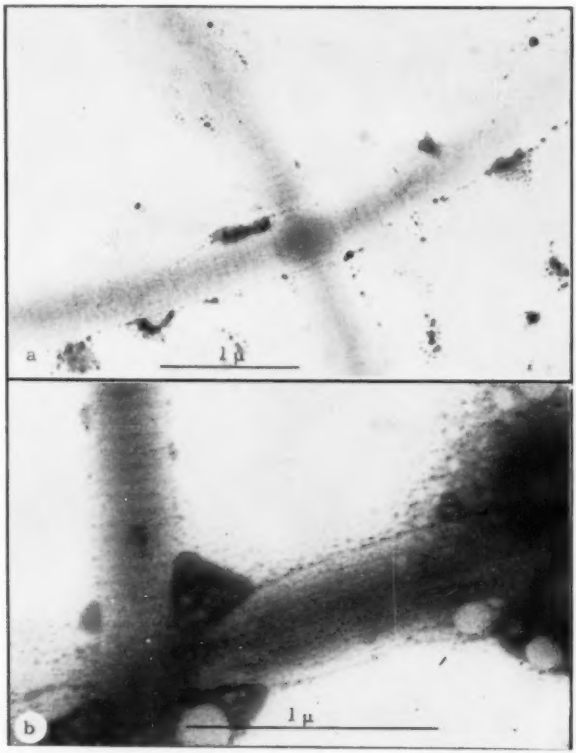

FIGURE 2.—Collagen Fibrils Treated with Lead Nitrate Solution. Fibrils were obtained from an unwashed reaction mixture.
a. Note the periodicity. Macroperiods average about 600 A. and consist of up to six intraperiod dark bands. 21,000 ×. b. Note the linear arrangement of particles parallel to the fibril axis. 38,250 ×.

lustrate the phenomenon of pseudostaining. Except for the fact that these fibrils are swollen, they have the appearance of *bona fide* electron-stained collagen illustrated in Figure 6. Electron density or contrast is high, and period and intraperiod structure is sharply defined. Until there was an occasion to use a nitric acid solution of lead nitrate, the impression was that collagen reacted with lead. However, in using an acid solution of lead nitrate in order to prevent acid attack upon the metal-supporting screens, electron microscope specimens were prepared by placing droplets of the acid reaction mixture on a Formvar film floating on the surface of a large volume of water. No evidence of lead could be found in specimens prepared in this manner. The lead had diffused through the membrane. Similarly prepared specimens

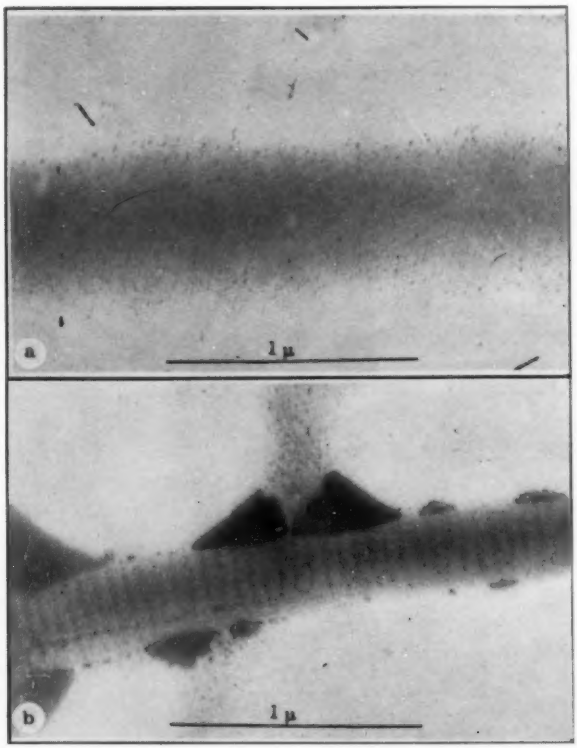

FIGURE 3.—Collagen Fibrils Treated with Lead Nitrate Solution. Fibrils were obtained from unwashed reaction mixture. 38,250 ×.
a. Note the linear arrangement of the particles transverse to the fibril axis.
b. Note the periodicity and the linear arrangement of the particles parallel to the fibril axis.

using aqueous lead nitrate solutions gave the same results. From these experiments it is concluded that the lead particles are adsorbed on the surface, in the micropores and crevasses, and along the edges of the fibrils, and do not react with the collagen.

The data presented thus far indicate that collagen will not react or combine with metal cations, metal-containing cations, or metal-containing anions in media having a pH in the range of 3.5 to 6.0. The cations Sr^{++}, Ba^{++}, Pb^{++}, and UO_2^{++} are lyotropic, cause collagen fibrils to swell, and lower the shrinkage temperature of the collagen.

The data pertaining to the treatments which produced positive results—namely, an increase in electron density of the collagen fibrils and no effect or an increase in the Ts of the collagen—are summarized in Table III.

TABLE III

SUMMARY OF DATA ON TREATMENTS WITH ELECTRON STAINS

Treatment	Ionic State of Metal	pH: Reagent Solution	pH: Reaction Mixture	Electron Staining*	Ts °C.†	Remarks
None (Control)	—	—	6.0	None	63	Cf. Figure 1a.
Chrome alum** $KCr(SO_4)_2$ (24)††	Cationic Nonionic Anionic	2.8	4.0‡‡	Positive	98	Cf. Figure 4
Phosphotungstic acid $H_3PW_{12}O_{40}$ (74)	$PW_{12}O_{40}^{3-}$ or $P_2W_{18}O_{62}^{6-}$	2.0	3.0	Positive	63	Cf. Figure 4a
Osmium tetraoxide OsO_4 (76)	$(OsO_4)^\circ$	5.0	5.0	Positive	78	Macroperiod = 640 A. (avg.)
	$(OsO_4)^\circ$	4.9***	4.9	Positive	78	Two electron-dense intraperiod bands characteristic.
	$(OsO_4)^\circ$	7.4***	7.4	Positive	78	
Uranyl acetate $UO_2(C_2H_3O_2)_2$ (92)	UO_2^{++}	4.5	4.6	Positive	73	Macroperiod = 600 A. (avg.)
	$[UO_2(C_2H_3O_2)_2]^-$ †††				93	Five to six electron-dense intraperiod bands. Ts 93° C. on acid-pretreated collagen (cf. text).
Plutonium in 1 *N* HNO_3 Pu (94)	$Pu^{IV}(NO_3)_4$ (ca 1.5%)	1.0	1.0	Positive	78	Macroperiod = 480 A. (avg.) Six electron-dense intraperiod bands. Cf. Figures 5 and 6b.
	$Pu^{IV}(NO_3)_4$ (ca 98.5%) †††					

*Electron staining refers to increase in contrast and definition of intraperiod bands.
†Ts = shrinkage temperature of collagen from washed reaction mixture.
‡Remarks = collagen from unwashed reaction mixtures usually overstained. Refers to collagen stained with diluted reagent solutions.
**Water of hydration excluded from formulae.
††Numbers in parentheses are the atomic numbers of the metal of interest.
‡‡After neutralization with $NaHCO_3$.
***Osmium tetraoxide buffered with sodium veronal, adjusted to pH with hydrochloric acid.
†††Cf. reference 4.

The data in Table III demonstrate the following: in all instances excepting the osmium tetraoxide, the metal of interest is part of an anionic complex; the pH of the reaction mixture is closer to the pH of the reagent solution than to that of the collagen dispersion; the electron-staining reactions were positive; and with the exception of the phosphotungstic acid treatment, the collagen from washed reaction mixtures had a higher Ts than untreated collagen.

With the exception of osmium tetraoxide, which is nonionic and will be discussed separately, compounds which produced positive results form complex ions when dissolved in water or acids. The ionic complexes may carry a positive or negative charge, or no charge at all. All three species may exist in the same solution, although the anionic complex is the important species. The pH of the reagent solutions and reaction mixtures are all below pH 5.0. In these reaction mixtures collagen carries a net positive charge, and complexes exist where metals are part of anions; therefore, conditions are favorable for the combination of collagen with the anionic complexes containing the metals. If this is so, the incorporation of the metal in the collagen fibrils will increase the electron density of the fibrils. The electronoscopic observations summarized in Table III and illustrated in Figures 4, 5 and 6 are evidence in support of the supposition.

The fact that the pH values of the reaction mixtures are closer to the pH values of the reagent solutions than to those of the collagen dispersion also indicates reaction of the collagen with the metal-containing complexes. With the nonreactive compounds pH changes caused by treatments can be ascribed to a dilution effect.

Collagen fibrils when treated with any of the reagents listed in Table III are invariably electron-stained. It makes no difference if the fibrils are from unwashed or washed reaction mixtures. The treated fibrils always have greater electron density than nontreated fibrils. One-percent solutions of the reagents frequently overstain the fibrils and obscure periodic structure. For optimal staining results, lower concentrations, usually 0.1%, were used. In staining with uranyl acetate, only three parts of uranium per thousand parts of collagen are required.

The osmium tetraoxide is nonionic but reacts with double bonds, terminal amino groups, non-peptide-NH groups, terminal hydroxyl groups, and many other reactive groups of organic compounds (5). Such reactive groups are present in collagen, and therefore the combination of collagen with osmium tetraoxide is independent of the pH of the medium.

Figures 4a and 4b illustrate formaldehyde-fixed collagen treated with 3% chrome alum liquor before and after neutralization with sodium bicarbonate. Formaldehyde-fixed collagen gives the same staining reactions as unfixed collagen but does not swell. Use of formaldehyde-fixed collagen eliminates the need for sodium chloride as a swelling inhibitor. The collagen obtained from the chrome alum reaction mixture before neutralization and washing

(Figure 4a) is pseudostained. The chrome precipitates out as a film along the edges and over the surface of the fibrils. Evidence of chrome was not found in washed preparations. The collagen from the neutralized reaction mixture after washing (Figure 4b) has high electron density and clearly defined intraperiod striations. The phenomenon of chrome tanning is explained as follows: At pH 2.8 there is an equilibrium established between the different types of ionic chrome complexes. On addition of the neutralizing agent ($NaHCO_3$) the equilibrium is upset, releasing anionic chrome complexes to react with the collagen. Similar results to those shown in Figure 4a are obtained if the staining compound is dissolved in citrate buffers, or if a chelating agent, such as disodium ethylene diamine tetraacetate (Na_2EDTA), is present in the staining solution or collagen dispersion (6).

The collagen fibrils shown in Figure 6a were stained with phosphotungstic acid. The macroperiod averages 650 A. There are six intraperiod dark striations in each macroperiod. As yet no investigator has been able to determine the significance of the intraperiod dark striations, other than to speculate that they represent loci of high concentrations of basic amino acids in the collagen molecule. The light bands represent loci of high water content. This is reasonable in that, if electron-stained collagen is shadowed, the stained portions or bands are the hills and the nonstained portions are the valleys of the fibrils as shown in Figure 1b. Dehydration *in vacuo*, during the shadow-casting process, removes water from the light bands causing these portions of the fibril to shrink. This is added evidence that the positively charged free amino groups (pH below 5.0) of the basic amino acid side chains of the collagen combine with the metal-containing anionic complexes of the staining compound. Phosphotungstic acid–stained collagen is an excellent example of electron staining. Contrast or electron density is greatly enchanced and intraperiod structure is clearly defined.

Attempts to determine a definite staining pattern for the different electron stains have thus far been unsuccessful. With the possible exception of osmic acid, which usually emphasizes only two intraperiod bands, the other stains emphasize two, five, six, and even ten intraperiod bands (7).

One of the principal objectives of this study was to determine the reactivity of collagen with plutonium. The metal will remain in solution only in acid solutions of pH 2.0 or lower, or special buffers. In 1*N* HNO_3 plutonium is 98.5% cationic and 1.5% anionic (4). When the acid plutonium solution is added to a collagen dispersion, the collagen swells because of the acid and the heat evolved from the mixing of acid and water. This effect is illustrated in Figure 5. Ordinarily, collagen fibrils heated in water above their shrinkage temperature swell markedly, and an electron-dense backbone having a convoluted or spiral configuration is formed (8). The fibrils also break up into short lengths. Fibrils treated with acid alone split into longitudinal components called filaments. The backbone in plutonium-treated collagen is

straight, and the fibrils are not broken into short lengths. In favorable micrographs period structure can be noted (Figure 5b). The Ts of such collagen is more than 65°C. The Ts of nitric acid–swollen collagen is so low that it cannot be determined. Shrinkage is noted the instant heat is applied. The electronoscopic appearance and the Ts of plutonium-treated collagen are not affected even after three months storage at room temperature in 0.1*N* HNO_3 solution. This is remarkable, as untreated collagen fibrils split up into their component filaments and will have a Ts of only 55°C. if allowed to soak in water at room temperature for as short a time as three days. Therefore, it is concluded that the swelling of the collagen when treated with acid solutions of plutonium is more an effect of heat than of acid. Furthermore, the plutonium fixes the collagen fast enough to prevent further degradation of the fibrils by acid.

Swelling of collagen can be prevented by the addition of salt or by fixation with formaldehyde. Neither method prevents electron staining. The collagen illustrated in Figure 6b was obtained from a reaction mixture originally containing 10% NaCl to inhibit swelling. Period and intraperiod structure is sharply defined. The macroperiods average 480 A. and consist of six dark intraperiod bands. Similar observations were noted for formaldehyde-fixed collagen treated with plutonium nitrate solutions. The smaller-than-normal macroperiodicity is ascribed to shrinkage during the reaction of the collagen with the plutonium. Shrinkage is a common phenomenon in electron-stained collagen. None of the effects noted for plutonium-treated collagen can be ascribed to radioacitivity.

Briefly, metal-containing compounds when dissolved in water or acid dissociate to form anionic complexes containing the metal, and if the pH of the medium is below pH 5.0, they will combine with collagen to increase the electron density of the collagen. Metal-containing compounds (OsO_4) which are capable of reacting with specific reactive groups (–HC=CH–, terminal –OH, free $–NH_2$, non-peptide-NH) of collagen do so regardless of medium pH.

The next factor to be considered is the effect of electron stains on the Ts of collagen. The Ts data are summarized in Table III. In all instances excepting the phosphotungstic acid treatment, there was an increase in the Ts. This means that the anionic complexes of chromium, uranium, and plutonium react with collagen to form additional crosslinks between the polypeptide chains of the collagen fibrils. These crosslinks are very strong and cannot be removed by prolonged washing with water. The stained fibrils do not split into filaments when treated with dilute acids. When heated in water above its Ts, electron-stained collagen fibrils first break up into short finite lengths, then proceed to swell in a manner similar to untreated fibrils. It is interesting to note that when salt- and acid-pretreated collagen is stained with uranyl acetate, the Ts is increased to 93°C. The fact that phosphotungstic acid has no effect on the Ts of collagen is ascribed to the reaction of only the free amino

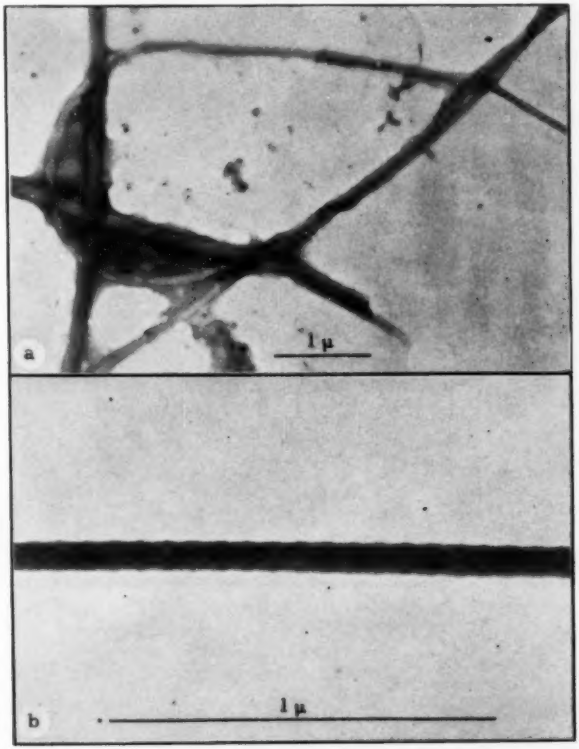

FIGURE 4.—Formaldehyde-fixed Collagen Fibrils Treated with 3% Chrome Alum Liquor. a. Fibrils obtained from unwashed reaction mixture, pH 2.8. Note that the chrome precipitates out along the fibril edges and on the fibril surfaces to give a pseudostaining effect. 15,000 ×. b. Fibril obtained from reaction mixture after neutralizing to pH 4.8 with sodium bicarbonate and after washing. Fibril is electron-stained. 59,000 ×.

groups of basic amino acid side chains of the collagen with the tungsten-containing anionic complexes.

Metal-containing compounds, which in solution dissociate into ordinary ions, will have no effect on the electron density of collagen; in fact, many of these ions are lyotropic and swell collagen. On the other hand, metal compounds, which in solution dissociate into anionic complexes containing the metal, do increase the electron density and with few exceptions raise the Ts of collagen.

These results are interpreted as signifying that metallic elements in their simple ionic form, or as constituents of simple ions, will not react *in vivo* with the organic matrix constituents (chiefly collagen) of skeletal tissue. There-

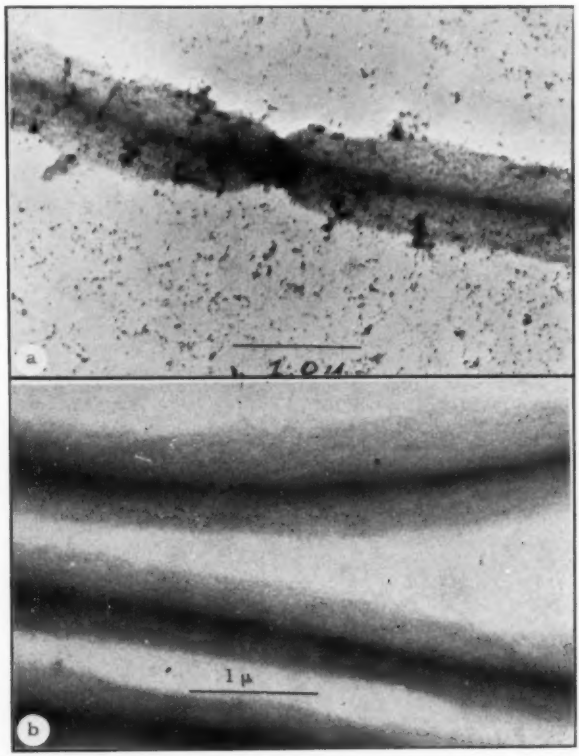

FIGURE 5.—Collagen Fibrils Treated with Plutonium in 1 *N* HNO_3. 19,500 ×.
a. Note period structure. Dense particulate matter in the background is probably plutonium oxide or hydroxide. b. Note the densely stained straight backbone. Close inspection of the backbone reveals periodic structure.

fore strontium, barium, tungsten as part of the WO_4^{--} ion, mercury, lead, and uranium as part of the uranyl $(UO_2)^{++}$ ion, or any metal in the form of, or as a constituent of, a simple ion, when introduced by ingestion or injection into the animal body, will become associated with the inorganic complex of skeletal tissue. This type of association lends itself to therapy with chelating agents.

On the other hand, compounds which dissociate to form anionic complexes of which the metal is a part can and do react *in vivo* with the collagen of skeletal tissue, forming a very stable compound. Such association does not lend itself to the chelating-agent therapy. This may be the reason why plutonium is so extremely difficult to remove from the body once it is established in bones.

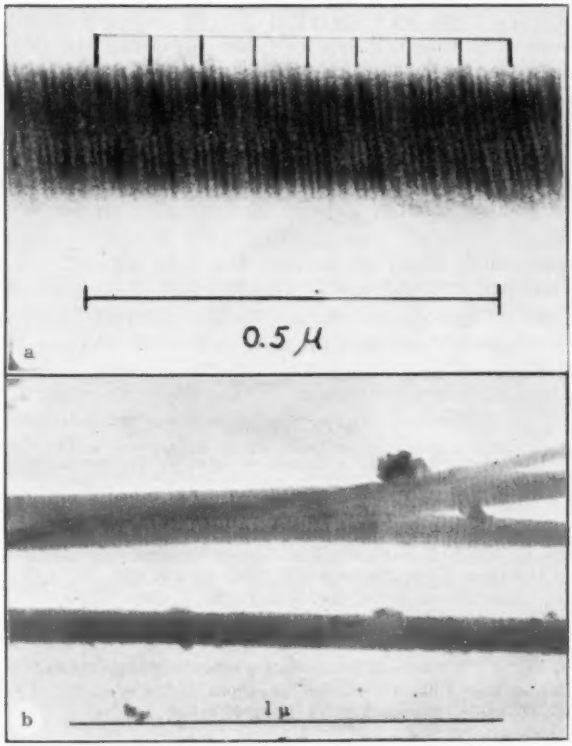

FIGURE 6.—Electron-stained Collagen.
a. Collagen fibrils stained with phosphotungstic acid. Note six clearly defined intraperiod dark striations. Macroperiod=640 A. (avg.). 127,500 ×. b. Collagen fibrils stained with plutonium in 1 *N* HNO_3. Sodium chloride (10%) was added to the dispersion to prevent swelling. Fibrils were obtained from washed reaction mixture. Macroperiods measure about 480 A., and consist of up to six intraperiod dark striations. 66,000 ×.

Osmium establishes itself in the organic matrix of bone tissue via reaction with specific groups, triple and double bonds, terminal hydroxyl groups, and terminal amino groups of the organic constituents (proteins, lipids, *et al.*) of skeletal tissue. The anionic complexes combine with positively charged free amino groups of the collagen in an acid medium (pH below 5.0) to form cross-links between the collagen polypeptide chains, to give a stable collagen-metal compound. Metal-containing compounds, such as osmium tetraoxide, which are nonionic but which will react with specific reactive groups of collagen, may be useful as tanning agents.

SUMMARY

1. The effects of treating collagen with solutions of thirteen different metal-containing compounds were studied by electronoscopic methods and Ts measurements.
2. Metals in the form of, or as part of, simple ions do not combine with collagen.
3. Metals as part of anionic complexes combine with collagen to give the collagen greater electron density and usually greater hydrothermal stability.
4. Metal compounds which are nonionic but react with -C = C-, terminal amino, terminal OH, and non-peptide-NH groups combine with collagen to give the collagen greater electron density and hydrothermal stability.
5. The significance of these results relative to deposition of metals in skeletal tissue and in explaining a mechanism of mineral tannage was discussed.

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Charles A. Martin of E. Hubschman and Sons, Inc., Philadelphia, Pa. has been appointed to the industry advisory committee on leather at Lowell Technological Institute for a three-year term. Also serving as advisers in the LTI Department of Leather Engineering are Dominic Meo, Salem Oil and Grease company, Salem, Mass., chairman of the committee; Malcolm H. Battles, A. C. Lawrence Leather Company, Peabody, Mass.; Erhard H. Buettner, Pfister and Vogel Tanning Company, Milwaukee, Wisc.; Charles T. Cares, John Flynn and Sons, Inc., Salem, Mass.; Lawrence Jones, Willard Helburn, Inc., Peabody, Mass.; and Louis E. Stahl, The Stahl Finishing Company, Peabody, Mass.

We have many pieces of skin and leather from the Egyptian tombs in a state of perfect preservation, which passed through the hands of the tanner more than thirty centuries ago, and which, but for the invention of this process, must have perished in a few hours after they had left the carcasses from which they were stripped.
—*Leather Manufacture*. John W. Stevens. Chicago: The Shoe and Leather Review, 1890.

THE EFFECTS OF FUNGICIDES ON DETERIORATION OF LEATHER*

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ABSTRACTS

The stability of chlorine-containing fungicides was studied by observing the amounts of Cl^- released in a benzene-HNO_2 mixture at 80° C. The stability under these conditions was presumed to give an indication of their stability in leather. Among nine fungicides studied, the amount of Cl^- released ranged from 0 to 13% of the total chlorine content. Eight of the compounds were chlorophenols. The liberation of Cl^- from chlorophenols appears to be facilitated by electronic effects that increase the electron density on the carbon to which chlorine is attached.

The effects of various fungicide treatments on leather deterioration under accelerated aging conditions were also investigated. Organically bound copper, chlorine, or chloride ions are less harmful to leather than copper or iron ions. There are some indications, however, that fungicides containing organically bound copper or chlorine may not be completely harmless.

INTRODUCTION

Recent reports from this laboratory have discussed the effectiveness of various compounds as leather fungicides (4,5,6). In connection with this work the question as to what effect a given fungicide treatment might have on leather deterioration, apart from its effect on mildew growth, naturally presents itself. Obviously, a treatment that is harmful to leather in any way should not be used, regardless of its potency as a mildew preventive.

According to findings by Lollar (12), who has recently reviewed leather deterioration (11), the presence of para-nitrophenol is not a major factor in such deterioration. Information about other compounds that might be used as fungicides is not available. In this respect it seemed desirable to investigate fungicides that contain copper and chlorine because of the known deteriorating action of inorganic materials containing these elements. Kan-

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agy (8) and also Hall and Mitton (7) have shown that salts of copper (and iron) are harmful to leather. Wilson (15) found that small amounts of hydrochloric acid cause leather deterioration and that high concentrations of chloride ions, even in neutral medium, are harmful.

It might be supposed that organic compounds containing these elements would also promote leather deterioration either directly or by liberation of the respective ions. Organic compounds containing varying percentages of chlorine, e.g., chlorophenols with from one to five chlorine substituents, comprise an important group of fungicides. Harmful effects of these compounds might depend on decomposition reactions that might be measured by the chloride ions liberated. It appeared simplest to study the chlorine stability of the compounds before impregnation in the leather but under conditions resembling those prevailing in leather. Since most leathers have pH values of about 3 to 4, and air oxidation is a factor in leather aging, study of the decomposition of chlorophenols under acid, oxidative conditions was undertaken. Subsequently investigations were made on the effect of treatments with various fungicides, some of which contained copper or chlorine, on leather deterioration under accelerated aging conditions.

RELEASE OF CHLORINE IONS FROM FUNGICIDES CONTAINING CHLORINE

There are reports in the literature of liberation of chloride ions by treatment of chlorophenols with nitric acid, with oxidation of the phenol to benzoquinones (1,13). This treatment was used in the investigation reported here. The amounts of Cl^- released under alkaline and neutral conditions were also observed for comparison.

Experimental details

(*a*) *Acid oxidative conditions.*—One gram of the fungicide was placed in a 250-ml. Erlenmeyer flask and dissolved in 75 ml. of benzene, after which 10 ml. of 6*N* nitric acid were added. The flask was heated at about 80° C. on a steam bath for one hour, with frequent shaking. After cooling, the reaction mixture was extracted with benzene, and the chloride ion in the aqueous solution was determined by Volhard's method (10).

(*b*) *Neutral conditions.*—One gram of the fungicide, 75 ml. of benzene, and 10 ml. of distilled water were placed in a 250-ml. Erlenmeyer flask. Three of the phenols used in these experiments were supplied as the sodium salts and, consequently, were insoluble in the mixture. They were dissolved by the addition of acetic acid in slight excess over the theoretical equivalent amount required for 1 gram of the phenol salt. After heating and cooling, 10 ml. of 6*N* nitric acid were added, and the separation and determination of chlorine were made as described in (*a*) above.

(*c*) *Alkaline conditions.*—One gram of the phenol, 50 ml. of 95% ethanol, and 10 ml. of 6*N* sodium hydroxide were placed in the flask and heated as described in (*a*). After cooling, 20 ml. of 6*N* nitric acid and 75 ml. of benzene were added, and the procedure was continued as in (*a*).

Results and discussion

In Table I the fungicides used in this experiment are listed in the order of increasing amounts of Cl^- ions released by the nitric acid treatment. Under neutral conditions only small amounts of Cl^-—in all cases less than 1%—were found. These amounts might very well have been due to chlorine-con-

TABLE I

RELEASE OF Cl- FROM FUNGICIDES CONTAINING CHLORINE

No.	Fungicide	Theoretical Cl-* %	Cl- Released: Acid Condition (HNO_3) Amount %	Acid Condition (HNO_3) Yield† %	Neutral Condition Amount %	Neutral Condition Yield† %	Alkaline Condition Amount %	Alkaline Condition Yield† %
1	2,4,5-trichlorophenyl acetate	44.4	0.00	0.00	0.00	0.00	2.8	6.3
2	tetrachlorohydroquinone	57.2	0.12	0.21	0.00	0.00	5.1	8.9
3	N-(trichloromethylthio) tetrahydrophthalimide	35.4	1.60	4.5	0.88	2.5	29.6	83.6
4	2-chloro-4-nitrophenol	20.4	1.65	8.1	0.10	0.50	0.2	1.0
5	chloro-2-phenyl phenol (4 & 6 chloro, mix.)	17.4	5.4	31.0	0.14	0.80	2.1	12.1
6	pentachlorophenol	66.6	9.3	14.0	0.60	0.90	0.7	1.0
7	4-chloro-3,5-dimethylphenol	22.7	10.8	47.6	0.00	0.00	0.07	0.31
8	2,4,5-trichlorophenol	53.9	13.1	24.3	0.32	0.61	1.4	2.6
9	2,3,4,6-tetrachlorophenol	61.2	13.4	21.9	0.95	1.5	1.1	1.8

*Percent by weight, assuming pure compounds. (Actually all these fungicides contained impurities.)
†Percent yield = (% Cl- released/% theoretical Cl-) X 100.

taining impurities, for none of these compounds were highly purified. Under alkaline conditions there were also comparatively small amounts of Cl^- liberated except in the case of N-(trichloromethylthio)tetrahydrophthalimide. This compound, from which nearly the theoretical chlorine content was recovered as Cl^-, appears to be quite unstable under alkaline conditions.

The data obtained under acid conditions are those of primary consideration in this investigation, and the following discussion is restricted to them.

Apparently there is no correlation between the total chlorine content, given in the first column of the table, and the amount of Cl^- released. In other words, the amounts of Cl^- released depends more on where the chlorine substituent is located in the organic molecule than on the total chlorine

content. The last five compounds listed in the table are phenols with a chloro substituent in the para position. It may be observed that the percent yeild decreased with increasing substitution of chlorine on other ring carbons. Apparently the para chlorine atom is the one preferentially released by the nitric acid treatment, which agrees with reports in the literature with respect to 2,4,6-trichlorophenol (1).

Most of the polychlorophenols apparently were oxidized to quinones by the acid treatment, as indicated by the formation of colored reaction products which were soluble in benzene. Chlorobenzoquinones appear to be stable as shown by the data for tetrachlorohydroquinone, which presumably is easily oxidized to the quinone.

It seems logical that a reaction that results in the release of chloride ions should be facilitated by any influence that tends to increase the electron density of the ring carbon to which the chlorine substituent is attached. The results obtained in these experiments are in accord with this. Thus, the ortho- and para-carbons of a phenol should be the ones with the highest electron density because of the electropositive inductive effect of the phenol group and the resonance effect which reinforces it (14). Acetylation of the phenol group probably inhibits or reduces these effects and thus stabilizes the chlorine substituents even in the orthopara positions as shown by the results for 2,4,5-trichlorophenyl acetate. It is interesting that esterification of the phenol groups also generally reduces mildew-preventive potency (6).

The results obtained for 4-chloro-3,5-dimethylphenol and 2-chloro-4-nitrophenol can be explained in a similar manner. About 50% of the total available chlorine was released as Cl^- with the former compound, while with the latter the corresponding percentage was only about 8. The electropositive methyl groups adjacent to the chlorine group in 4-chloro-3,5-dimethylphenol could be expected to increase the electron density of the *p*-carbon and facilitate Cl^- release. The electronegative nitrate group, on the other hand, would tend to stabilize the chlorine in 2-chloro-4-nitrophenol, since electrons are attracted away from all ring carbons.

Wilson (15) found that in treating samples of a vegetable-tanned leather with solutions of HCl varying in strength from 0.1*N* to 5.0*N*, drying, and aging for 46 days, 0.033% HCl would be retained regardless of the strength of the treating solution. All samples showed a loss in tensile strength of about 25%. Other investigators (2) have found that leather is severely damaged by 0.1*N* HCl, even more so than by higher concentrations. Data on the effect of small amounts of chloride ions under neutral conditions are not available. However, as has been mentioned, Wilson (15) found such ions very destructive if present in high concentration, in contrast to sulfate ions which appeared to have a preservative effect.

If we assume that a leather contains 1% of a fungicide which in aging decomposes to the extent of 2% as chloride ions, the concentration of the

latter would be 0.02%. Four of the nine fungicides listed in Table I liberated less than 2% chloride ions under the exaggerated leather-aging conditions represented by the nitric acid treatment. The other five fungicides liberated from 5 to 13% chloride ions.

In Table I the fungicides are ranked in decreasing order of chlorine stability. If chloride ions are produced in leather and are destructive, the effect of these fungicides on leather deterioration should rank them in a corresponding order. The effect of some of these compounds on leather deterioration will be discussed in the following section.

EFFECTS OF VARIOUS TREATMENTS ON DETERIORATION OF LEATHER

Seventeen fungicides, some of which contained chlorine or copper in organic combinations, were impregnated into tensile-strength specimens of leathers by treatments with solutions of the fungicides in organic solvents. Similar specimens were treated with aqueous solutions of copper sulfate, copper acetate, sodium chloride, ferrous sulfate, water alone, and solvents alone. The fungicides were chosen more or less arbitrarily as representative of the types of compounds that have been screened as leather fungicides in this laboratory (6). They include most of the chlorine-containing fungicides discussed in the previous section of this report. The copper and iron salts were included as representatives of known deteriorating treatments, and sodium chloride for observing the effect of chloride ions in neutral solution. After treatments and drying, the leather specimens were exposed to accelerated aging for 7 days in a slow current of air maintained at 100° C. and 12% relative humidity. Untreated leather specimens were exposed to the same aging conditions.

After reconditioning for several days at 23° C. and 50% relative humidity, the tensile strength of the specimens and percent stretch under breaking load were determined according to Methods 2011 and 2021 of Federal Specification KK-L-311a, January 19, 1953. The losses of strength and stretch on aging of treated specimens compared to losses by untreated ones were used as the criteria for treatment effect on leather deterioration.

Experimental details

Leathers.—The leathers used in this study were:

1. Military-type chrome-tanned upper leather containing about 4.5% chrome per 100 hide substance, as Cr_2O_3 and 30% grease. Pieces 12 x 12 inches available from a previous study were used. They were from different hides and hide locations. Eighteen tensile-strength specimens could be cut from each piece, and these were divided at random into six sets of three specimens each. One set was not treated and not aged, and one set was not treated but aged, leaving four sets of specimens from each piece of leather

available for four different treatments. Since this leather was nearly impervious to water, it was not used for treatments requiring an aqueous medium.

2. Vegetable-tanned strap leather. This leather contained about 12% grease but was quite permeable to water as well as to organic solvents; it was used with both types of treatments. As with the chrome-tanned leather, sets of three specimens each picked at random were used for one test of each treatment. Large pieces of this leather were available so that all specimens required for one test could be cut from the same piece. This piece was taken from the middle portion of a side (half hide). The tensile strength specimens from both leathers were cut perpendicular to the backbone.

Treatments of specimens before aging.—The fungicides and salts were impregnated into the leathers by immersion into organic solvent solutions of the former and aqueous solutions of the latter. The solution concentration of all fungicides was 3%. The amounts of solution absorbed by the specimens were determined by weighing before and immediately after treatments.* From this the average deposition of fungicide in the chrome-tanned leather (20% absorption) was calculated to be 0.6%, and in the vegetable strap leather (80% absorption), 2.4%. The solvent used in preparing the solutions was a mixture of cyclohexanone, mineral oil, and trichloroethylene. With most fungicides the ratios of these solvents as weight percentages were 10, 20, and 70. In a few cases more cyclohexanone and less trichloroethylene had to be used to obtain complete solution. Aqueous solutions of the salts, cupric sulfate, cupric acetate, ferrous sulfate, and sodium chloride, were of such concentrations that approximately 0.4% of Cu, Fe, or Cl would be deposited in the vegetable leather, calculated from solution absorption.

Accelerated aging.—The accelerated aging of the leather specimens was conducted essentially as described by Kanagy (9) except that a vacuum oven was used as the exposure chamber. The specimens were supported in a vertical position by stringing them on wires fastened to a frame that fitted the inside of the oven. A puncture was made for the wire through one end of the specimen near the edge. A slow current of air from an air line was passed through the oven. Before the air entered the oven, it was bubbled through a series of four saturators containing distilled water. The saturators were placed in a temperature-controlled water bath. The air flow was measured with a flow meter as it emerged from the oven.

Preliminary tests with untreated samples of the leathers showed that about 50% loss in tensile strength occurred when the specimens were exposed in the oven at 100° C. for 7 days, and the air, flowing at a rate of about

*As pointed out later, the organic solvent leached out some of the grease from the heavily stuffed chrome leather, and therefore the actual percentage of fungicide introduced was somewhat larger than the percentage figured from the net gain in weight. The percentages of fungicide introduced were considerably higher than the quantities normally used in practice.

0.02 cubic feet per hour, was saturated with water at 50° C. The atmosphere in the oven should then have about 12% relative humidity.

These conditions were suitable for detection of variations in deterioration by the various treatments and were used for all the experiments reported in this investigation.

Calculation of loss on aging of strength and stretch.—The following formula was used for calculating the loss on aging of each of these properties due to the various treatments:

$$\text{Loss on aging} = \frac{A - B}{A - C} \times 100$$

where A = average tensile strength or average percent stretch at breaking load of untreated, unaged leather

B = average tensile strength or average percent stretch at breaking load of treated, aged leather

C = average tensile strength or average percent stretch at breaking load of untreated, aged leather

Tensile strength and percent stretch at breaking load was determined on the same specimen. Each average in the formula above included measurements on three specimens, and the whole expression yielded one single test value for the effect of a treatment. Losses on aging less than 100 denote that a treatment had a preservative effect. Losses over 100 denote a deteriorating effect.

Results and discussion

The effects of the various treatments on tensile strength and stretch, calculated as described above, are given in Figure 1 for each of the two leathers used. Duplicate tests were made with all treatments, and the average test results were plotted as shown. The 95% probability limits at the bottom of the figure were calculated from the differences of duplicate test results. The meaning of the probability limits is that on the average only one experimental value out of twenty should fall outside the limits by chance. Therefore, the probability limits centered on 100 indicate whether or not the observed effects are significant at the 95% level.

The treatments are listed in the order of increasing deteriorating effects as indicated by loss in tensile strength and are based on the average results for both leathers. The loss in tensile strength is thought to be a better criterion of deterioration than loss in stretch. The latter measurements are subject to very large experimental errors, particularly with weak specimens.

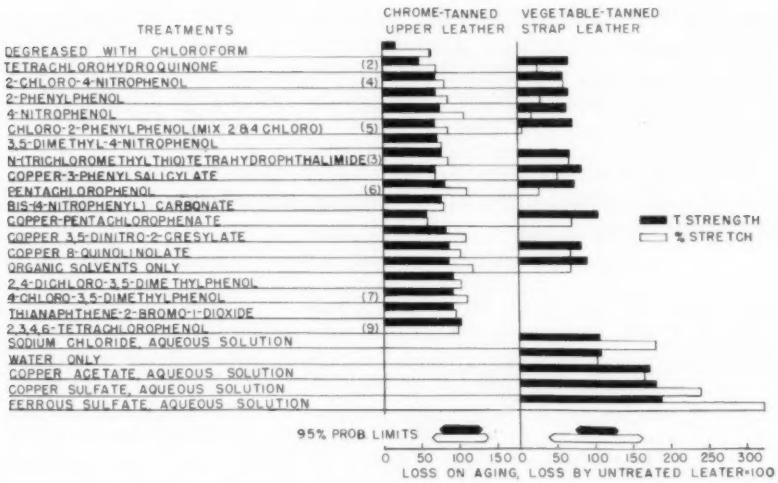

FIGURE 1.—The effects of treatments on strength and stretch as revealed by accelerated aging. Numbers in parentheses indicate order of ranking according to amount of chloride ion released, as listed in Table I.

It may be seen that only the last three treatments listed, aqueous solutions of copper acetate, copper sulfate, and ferrous sulfate, had significant deteriorating effects. As already mentioned, these treatments were known to promote leather deterioration and were included as controls. Accordingly, none of the fungicide treatments caused any deterioration. On the contrary, most of these appeared to have a preservative effect, as did treatments with the organic solvents mixture only. The inactive formulation components probably are responsible for this in the following manner: Since the formulations contained 20% mineral oil, additional lubricant would be deposited by the treatments in the vegetable strap leather that originally contained about 12% grease. Reduced fiber friction resulting from more complete lubrication could be expected to increase both strength and stretch in accordance with the experimental results. The chrome upper leather, on the other hand, contained about 30% grease, and some of this undoubtedly would be removed by the treatment with the organic solvent formulations. Excessive amounts of grease apparently promoted deterioration, as partial degreasing with chloroform before aging had a significant preservative effect, as shown in Figure 1. Bowker and Churchill (3) have reported similar observations under normal aging conditions. The accelerated aging conditions used in this study could be expected to magnify the deteriorating effect of excessive lubricant.

The general preservative effects observed with all treatments employing the organic solvent formulations thus appear to be caused by the addition of lubricant in the case of vegetable strap leather and by removal of excessive lubricant in the case of the chrome upper leather.

To some extent the preservative effect just described might have obscured any deteriorating effect of the fungicides. The four copper-containing fungicides that were included in this study appeared to have no harmful effect on the chrome upper leather. If they did, they would have been grouped at the bottom of the list. However, it may be observed that they did produce the greatest deterioration among the fungicides used in treatments of vegetable strap leather. This suggests that the vegetable tannage is somewhat sensitive to organically combined copper, although this experiment does not definitely prove that. Neither do the data obtained in this study give any definite indication that chlorine-containing fungicides are harmful. However, the ranking order of the chlorinated fungicides in Table I and Figure 1 is nearly the same. The ranking numbers in Table I are shown in parenthesis in Figure 1. This suggests that decomposition products of the fungicides may promote deterioration. Treatment with sodium chloride in aqueous solution, compared with treatment with water alone, apparently promoted loss in stretch but had no effect on strength.

CONCLUSIONS

The release of chloride ions from chlorine-containing fungicides under acid oxidative conditions varies greatly with different fungicides and is probably negligible with many. The para-chlorine of chlorophenols is easily released. Acetylation of the phenol group inhibits the release of chlorine even from the para position. The data obtained generally are in accord with what could be predicted by theoretical consideration of electronic effects.

Accelerated aging (7 days' heating at 100° C. in a slow current of air maintained at 12% relative humidity) has revealed no marked deterioration of leathers due to treatments with copper-containing fungicides in organic solvent-type formulations, contrasting in this respect to the effect of copper or iron salts in aqueous solutions. Neither chlorine-containing fungicides in organic solvents nor sodium chloride in aqueous solution produced any significant deterioration of leathers treated with these materials and subjected to the aging test. Apparently copper or chlorine organically bound or chloride ions are less harmful to leather than copper as copper ion. There are some indications, however, that organic compounds containing these elements may not be completely harmless. Their use as leather fungicides are not excluded but should be subject to some caution and further investigation where maintenance of leather strength for a long time is required.

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DISCUSSION

C. W. MANN (Quartermaster Research and Engineering Center): The author is to be congratulated on presenting this paper, as it illustrates the large amount of background that goes into development of a fungicide material.

One of the big objections to the use of most fungicides is that they contain groups which might theoretically volatilize some component that would damage an item in contact with the leather, as in the case of carrying cases used to contain optical instruments. There is a possibility that chloride compound might form hydrochloric acid and that a nitrate compound might form nitric acid. This report shows what can be learned from a study of the volatility of various components and at the same time goes into the possibility of damaging the leather with these materials.

There have been objections to the use of fungicides on leather based upon statements in the literature that the treatment of leather with fungicide causes damage to the leather. I think the figures showed that all the fungicides studied in this particular case caused less damage to the leather than the control specimens, which shows that there is a preservative effect on the leather.

Since this paper deals with the deteriorating effect on leather, I would like to show a sample of what happens if you do not use a fungicide. We

have stored shoes in the South Pacific warehouses, and I have a sample that was in storage for three years. (*Showing sample*). This was in the original packing case and has not been used. It was taken out of the case and considered unsatisfactory for use. It was badly molded. I would like to demonstrate what happens to leather under these conditions—you can tear it much like paper. It has lost more than half of its strength, and it is entirely unsuitable for use. I think you will agree that the deterioration reported today was relatively mild compared with this.

It must also have been early noticed that wood smoke, which in those days was inseparable from the use of fire, had an antiseptic and preservative effect on skins which were dried in it, and smoked leathers are still made in America, both by the Indians and by more civilized leather manufacturers. To this method the Psalmist refers when he says, "I am become like a bottle in the smoke" (Ps. cxix. 83); and such bottles, made of the entire skin of the goat, are still familiar to travellers in the East.

The process of dressing by rubbing and kneading with greasy matters is described in the *Iliad* (xvii. 389-393) in the account of the struggle over the body of Patroclus:

"As when a man
A huge ox-hide drunken with slippery lard
Gives to be stretched, his servants all around
Disposed, just intervals between, the task
Ply strenuous, and while many straining hard
Extend it equal on all sides, it sweats
The moisture out and drinks the unction in."

Leather manufacture reached considerable perfection in ancient Egypt. A granite carving, probably at least 4000 years old, is preserved in the Berlin Museum, in which leather-dressers are represented. One is taking a tiger-skin from a tub or pit, a second is employed at another tub, while a third is working a skin upon a table.

Another fact, which is scarcely understood by the practical man in his demands on science, is that in leather manufacture every question which is raised seems to rest on the most recondite problems of chemistry and physics; the chemistry of some of the most complex of organic compounds, and the physics of solution, of osmose, and of the structure of colloid bodies—problems which are yet far from completely conquered by the highest science of the day . . . A knowledge of chemistry will probably prove at least as important to the future of our trade as that of mechanics has been in the past.

—*The Principles of Leather Manufacture.* H. R. Procter. London: E. & F. N. Spon, Ltd., 1903.

LEATHER–FINISH–ADHESION TEST*

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ABSTRACT

Two new heat-set adhesives have been found which are suitable for use with the leather-finish-adhesion test. A phenolic bonding film, previously reported as the basis for this test, adheres well only to certain shoe upper leather finishes. The two new adhesives allow the test to be applied to practically all types of leather finishes.

A solvent-free, cold-set adhesive also has been found which adheres well at room temperature to most shoe upper leather finishes. Temperature effects on the test are thus minimized, and the adhesion values obtained with this adhesive are more realistic for some leather finishes than results obtained with the heat-set adhesives.

The heat-set adhesives are best adapted to control purposes, since sample preparation times are short. However, the inherent freedom from temperature effects makes the cold-set adhesive more valuable as a research tool.

INTRODUCTION

A method for measuring the adhesion of leather which gives quantitative results independent of other finish properties was reported previously by Battelle Institute under the title "The Bonding Film Adhesion Test for Leather Finishes" (1). The heat-activated phenolic film described in the original paper adheres to a number of shoe upper finishes but will not adhere to leathers top-coated with lacquer or vinyl. Therefore it appeared desirable to find other adhesives applicable to a wider range of leather finishes.

MATERIALS AND PROCEDURE FOR FINISH–ADHESION TESTS

Three new adhesives have been found which greatly widen the scope of the finish-adhesion test. Two of these are heat-setting adhesives used very similarly to the heat-activated phenolic film in previous work. A mixture of polyamides is applicable to nearly all shoe upper leathers. A vinyl chloride

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copolymer adheres to lacquer and upholstery leather finishes. The third new adhesive is an epoxy-based cold-set adhesive which adheres to practically all shoe upper leathers without heat or special equipment.

Polyamides.—A mixture of polyamide resins adheres to practically all present-day shoe upper leather finishes. The formulation used in this work is as follows:

Versamid 100*	3 parts by weight
Versamid 950*	2 parts by weight
Toluene (solvent)	15 parts by weight

This mixture is applied as a hot solution to a 1″-square area of 1″ x 3″ copper strip to give a film thickness of 2–4 mils. The polyamide-coated copper strip is thoroughly dried at 210° F. for 1 hour. It is then bonded to the leather finish surface at a block temperature of 140° C., 10–12 psi, and a dwell time of 15 seconds by means of the apparatus described in the previous paper (1).

Vinyl chloride copolymer.—The second new adhesive is a vinyl chloride–vinyl acetate copolymer. It adheres well to vinyl- and lacquer-finished upholstery leathers. The formulation used is as follows:

VAGH†	1 part by weight
Methylisobutylketone	3 parts by weight

The copolymer is dissolved in the solvent by heating. The hot solution is applied by brush to a 1″-square area of a 1″ x 3″ strip of 8-ounce cotton canvas and air-dried. A second layer of adhesive is then applied to the same area and dried at 120° F. for 1 hour. It is necessary to use canvas as backing for the vinyl chloride copolymer because it does not adhere satisfactorily to copper strips. The adhesive-coated canvas is then applied to the surface of the leather finish at a temperature of 160–170° C., 10–12 psi, and a dwell time of 30 seconds by means of the apparatus previously described.

Epoxy adhesive.—The formulation used for a cold-set, solvent-free epoxy adhesive for use with shoe upper leather finishes is as follows:

Resiweld Adhesive No. 1** (Part A)	2 parts by weight
Resiweld Hardener B-1** (Part B)	1 part by weight

The epoxy adhesive is prepared for use by weighing two portions of epoxy resin, part A, to one portion of resin-type hardener, part B, and mixing thoroughly. The quantity of catalyzed adhesive mixed must be used within 2 hours since this adhesive begins to set after addition of the hardener. The mixture is applied by spatula as a thin film to a 1″-square area of a 1″ x 3″

*Obtained from General Mills, Inc., Chemical Division, Kankakee, Illinois.
†Obtained from Bakelite Division, Union Carbide Corporation, Cleveland, Ohio.
**Obtained from H. B. Fuller Company, 181 West Kellogg Boulevard, St. Paul 2, Minnesota.

strip of 8-ounce cotton canvas. The adhesive-coated area is placed in contact with the finish surface of a leather strip of the same dimensions, placed on a sponge rubber sheet, and covered by a 1″-square brass bar to provide constant pressure between parts. Specimens are cured for 24 hours prior to testing for finish adhesion.

RESULTS AND DISCUSSION

The effect of bonding temperature on finish adhesion of several leathers as determined with the polyamide mixture as adhesive was studied, and the results are shown in Figure 1.†.

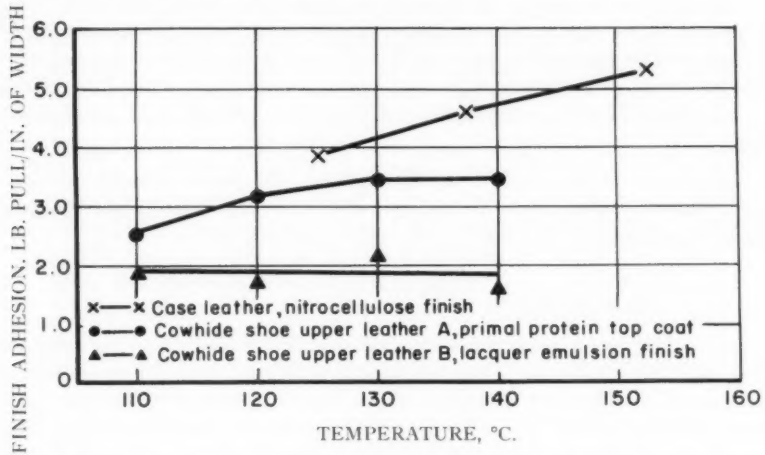

FIGURE 1.—Effect of bonding temperature on finish adhesion with the heat-setting polyamides as adhesive. (Specimens prepared at a bonding pressure of 10–12 psi and a dwell time of 15 seconds. Each point is based on 10 samples).

Visual examination of the adhesion-test specimens of case leather indicated that removal of the lacquer emulsion finish is more complete at a block temperature of 150° C. than at lower temperatures.

Specimens prepared at a temperature below 140° C. showed incomplete removal of finish from the leather. Therefore for this leather a temperature of 150° C. is necessary. The graph for cowhide shoe upper leather A indicates that a block temperature of 130°–140° C. is satisfactory for obtaining good adhesion; higher temperatures give higher adhesion values. A wide temperature range is satisfactory for cowhide shoe upper leather B. However, removal of the finish was in both cases more complete at a temperature of 140° C. Therefore, a block temperature of 140° C. is recommended for preparation of

†The data in all tables and figures (except Figure 3) were obtained using a Scott Tester Model L-6 at a pulling rate of 12 inches per minute.

adhesion specimens of cowhide shoe upper leathers with the polyamide mixture.

The effect of bonding temperature on finish adhesion with vinyl chloride copolymer as adhesive is shown in Figure 2. The graph for upholstery leathers A, B, and C shows that a fairly wide temperature range is satis-

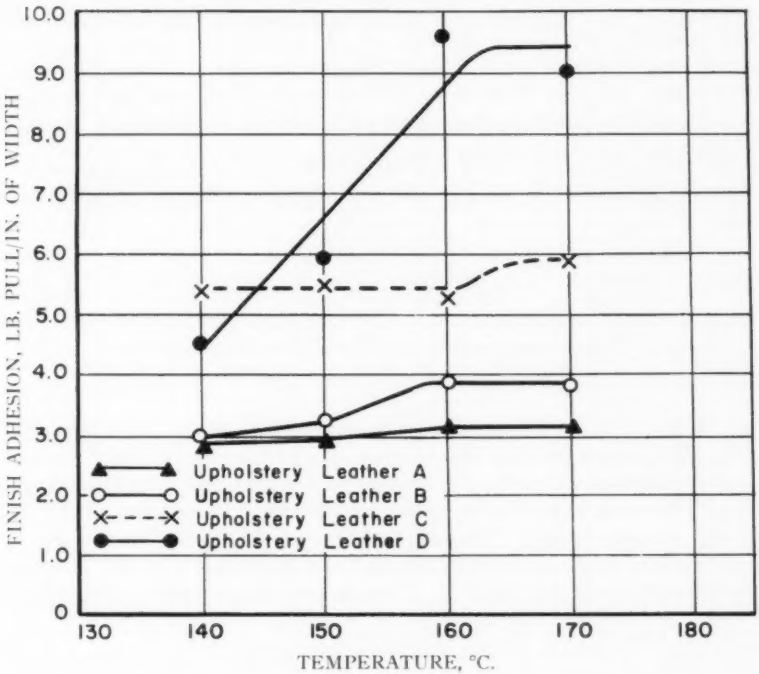

FIGURE 2.—Effect of bonding temperature on finish adhesion of upholstery leathers with the vinyl chloride copolymer as adhesive. (Specimens prepared at a bonding pressure of 10–12 psi and a dwell time of 30 seconds. (Each point is based on 10 samples).

factory since there were no significant differences in adhesion values at the temperatures studied. For leathers A, B, and C, reasonably good results were obtained at all temperatures employed; the temperature range of 160°–170° C. is necessary for upholstery leather D to obtain maximum lift of the vinyl finish from the leather. In general, for vinyl- and lacquer-finished leathers a temperature of 160°–170° C. for preparation of adhesion-test specimens is recommended with vinyl chloride copolymer as adhesive. A dwell time of 30 seconds is necessary for the preparation of the adhesion-test

specimens because of the poor heat-transfer property of the canvas backing used with this adhesive.

The question has been raised as to whether the temperatures used during the preparation of the adhesion-test specimens may cause fusion of the leather finish. This fusion could result in erroneously high adhesion values. The results of a comparison of the cold-setting epoxy adhesive, the phenolic bonding film, and the polyamide mixture are shown in Table I. The adhesion

TABLE I

COMPARISON OF ADHESIVES FOR THE FINISH–ADHESION TEST

Adhesive	Type	No. of Samples	Adhesion, lb/in*	
			Average	Standard Deviation
Epoxy	Cold-set	10	2.2	0.5
Phenolic	Heat-set	6	4.2	0.6
Polyamide	Heat-set	14	4.1	0.4

*Determined on chrome-tanned, heavily buffed cowhide shoe upper, black-pigment finish.

results given are for a commercially finished chrome-tanned shoe upper cowhide. The values indicate that the force required to lift the finish from the leather grain is the same for the phenolic bonding film and the polyamide mixture. However, the adhesion value is significantly lower when the cold-set epoxy adhesive is used. The effect of heat on the leather finish under the conditions of preparation of the adhesion-test specimens is further illustrated for different leathers in Table II. There is a significant difference in adhesion

TABLE II

COMPARISON OF ADHESION VALUES OBTAINED WITH COLD–SET AND HEAT–SET ADHESIVES

Leather	Adhesion, lb/in*			
	Cold-set Epoxy		Heat-set Polyamide	
	Average	Standard Deviation	Average	Standard Deviation
Cowhide, shoe upper, pigment finish	1.8	0.7	3.4	0.4
Cowhide, shoe upper, semianiline finish	1.7	0.9	1.7	0.3
Case, lacquer topcoat	3.8	1.25	4.6	0.4

*Each entry based on 10 samples.

values for the pigment-finished cowhide shoe upper. The heat effect is not evident for the semianiline-finished cowhide shoe upper leather because the base coat of the finish is presumably proteinaceous. Such a material does not fuse and is therefore not affected by the high temperature used in the preparation of the specimens. The difference in adhesion values exhibited by the case leather top-coated with lacquer probably is not significant because of the large standard deviation obtained with the epoxy adhesive. Therefore, the high temperatures used in the preparation of adhesion specimens with the phenolic bonding film and the polyamide mixture appear to increase the adhesion values of finishes formulated with resins of softening points lower than the temperatures used for the preparation of adhesion-test specimens.

The epoxy adhesive was compared further with phenolic bonding film on a series of experimental finishes. The results are shown in Table III where

TABLE III

ADHESION VALUES AND RANK OF EXPERIMENTAL LEATHER FINISHES

Sample	Adhesion, lb/in		Rank	
	Phenolic*	Epoxy†	Phenolic	Epoxy
1	3.7	2.6	1	1
2	6.8	3.8	2	2
3	10.0	4.1	3	3
4	10.8	6.0	4	5
5	11.65	5.2	6	4
6	11.5	7.6	5	6
7	15.6	9.9	7	7

*Based on 10 samples.
†Based on 3 samples.

the data are given in terms of absolute adhesion values and also by rank. Although the phenolic bonding film gives higher adhesion values in every case than the epoxy adhesive, the results when ranked in order of increasing value show a striking similarity. The two rankings, when correlated by Spearman's formula (2), give a calculated rank correlation coefficient of 0.893, which is significant at the 99% level. This means that there is less than a 1% probability of getting such good correlation by pure chance. It is felt that the absolute adhesion values obtained with the cold-set adhesive are probably more realistic than those obtained with the heat-set bonding film. However, since the two adhesives give such good correlation, it may be assumed that the bonding film gives the same relative results as the cold-set adhesive.

During the course of our investigation it appeared that when the finish-adhesion-test specimens were pulled apart and the adhesion values measured

on an instrument indicating maximum load, the registered values were too high. It was suspected that a component of the cohesion of the finish film was being measured in addition to its adhesion to the leather. Use of the Instron Tester permitted the detection and graphical recording of this phenomenon. Two curves obtained in determining the adhesion of a vinyl finish to an upholstery leather are shown in Figure 3. The vinyl finish was

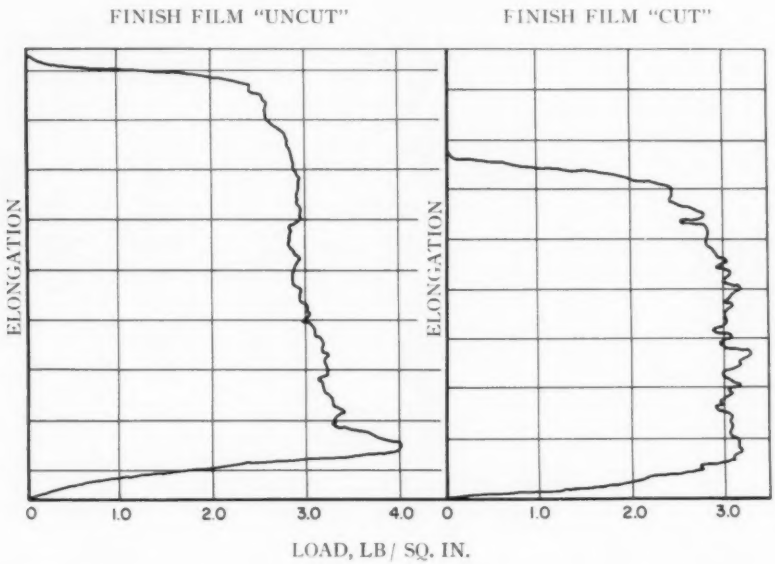

FIGURE 3.—Curves from measurement of the finish adhesion using the Instron Tester. (Determined on vinyl-finished upholstery leather.)

cut along the edge of the adhesive with a sharp blade prior to making the adhesion measurement for the curve on the right. It is evident that for the curve on the left the initial high reading of 4.04 pounds is a measure of the adhesion of the finish to the leather plus a component of the cohesion of the finish film. This would be the value recorded by an instrument measuring maximum load. The adhesion of the finish to the leather is registered at the lower load level of 3.0 lb. and is verified by the curve on the right where the finish film is cut. This represents the true adhesion of the finish to the leather. Therefore it is recommended that the finish along the edge of the adhesive be cut prior to testing the adhesion-test specimens. This is particularly important when an instrument measuring maximum load is used.

A number of other cold-set adhesives, epoxy-based and also other types, were evaluated for this adhesion test. However, none gave as good results as the epoxy adhesive selected and is considered satisfactory.

Several solvent-based adhesives were also evaluated for this adhesion test. The solvents employed as bases for this type of adhesive formulation partially dissolved the finish material and allowed the adhesive to penetrate through the finish to the grain layer, resulting in adhesion values higher than those obtained with the solvent-free cold-set and heat-set adhesives discussed previously.

SUMMARY AND CONCLUSIONS

The leather-finish-adhesion test is now adaptable to practically any type of leather finish (see Table IV). For quality-control purposes the heat-

TABLE IV

SUMMARY OF ADHESIVES SUITABLE FOR USE WITH THE LEATHER FINISH–ADHESION TEST

Leather	Top Coat Material	Adhesive
Cowhide shoe upper	Protein and lacquer emulsion	Heat-set phenolic bonding film Heat-set polyamide Cold-set epoxy
Case	Nitrocellulose	Heat-set vinyl chloride copolymer Cold-set epoxy
Upholstery	Vinyl	Heat-set vinyl chloride copolymer
Upholstery	Lacquer	Heat-set vinyl chloride copolymer
Goatskin glove	Acrylate	Cold-set epoxy

set adhesives probably are best adapted because they require relatively short times for specimen preparation. For this purpose the phenolic bonding film, the polyamide mixture, and the vinyl chloride copolymer are applicable, as long as the interpretation is restricted to the same general finishing system, particularly to those formulated from the same resin. These adhesives cover the complete spectrum of contemporary leather finishes.

The cold-set epoxy adhesive is adaptable to all but upholstery leathers top-coated with vinyl and lacquer. Temperature effects with this adhesive are eliminated, and the adhesion values obtained are more nearly "true" than results obtained with the heat-set adhesives. The inherent freedom from temperature effects makes the cold-set adhesive the more valuable as a research tool.

ACKNOWLEDGMENT

We wish to thank the Tanners' Council of America for its support of this work and for permission for publication. Suggestions and comments by Mr. E. B. Thorstensen, Dr. Ell Dee Compton, Mr. Allen Phillips, Mr. G. Alan Rothschild, Mr. H. K. Dugdale, and Dr. Fred O'Flaherty have been helpful.

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1. Burkart, C. A., N. D. Gallagher, and M. B. Neher. *JALCA*, **51**, 418–428 (1956).
2. Spearman, C. *Am. J. Psychol.*, **15**, 88 (1904).

Received July 8, 1957.

DISCUSSION

DR. ROBERT SHAW (Rohm & Haas Co.): Mr. Gallagher and his coworkers at Battelle are to be congratulated on the progress they have made on this subject since our last meeting. I think the most important improvement that has been made is the use of a cold-set adhesive, because with the hot-set adhesives we are actually measuring the adhesion of the finish under rather unusual conditions, temperatures of from 140° to 170°C. being considerably higher than most leathers are subjected to in the tannery.

From the data which Mr. Gallagher has presented, it is evident that there is a difference in the apparent adhesion with the hot and with the cold methods. It is a little unfortunate, I believe, that the standard deviation with the cold-weld cement is so much more in some cases than with the hot-weld, because I think the greatest improvement that could be made in this method would be to find a cold-weld cement that would give at least as low a standard deviation as the hot-weld cements.

With a method such as this, the degree of adhesion between the cement and the top surface of the finish must be definitely greater than the degree of adhesion of the finish to the leather. I was wondering whether you have carried on any work on films or finishes apart from leather, to see if this would show up?

MR. GALLAGHER: No, we have not, Dr. Shaw. All our work has been confined to leather testing. In general we find, though, that the strength of the bond between the adhesive film and the leather is much greater than the bond between the leather and the leather finish.

DR. SHAW: It is shown by your curves that you get a rapid increase in apparent adhesion after you go above 170°C. Why is this?

MR. GALLAGHER: That is probably due to heat effects on the finish causing fusion of the adhesive into the finish, and fusion of the finish into the leather.

DR. SHAW: On this difference between hot and cold bond, I wonder if an experiment of the following type has been made (it probably could be run easily, since you now have a cold-setting cement). Take a piece of finished leather and subject part of it to the temperature and pressure which you use with your heat-set weld; then take this piece and an adjoining piece and test both of them with the cold-set cement to see if a difference shows up in the apparent adhesion.

MR. GALLAGHER: That has not been done, but such an experiment would be interesting.

DR. SHAW: One other thing is that when you test the adhesion of a finish, by a regular hand test, you generally find that on a very heavily coated leather the adhesion appears to be worse than on a leather that is very lightly coated. This is probably because of the greater strength of the heavy film. With a light coating the film tears and does not appear to peel. Now with the type of apparatus you use, this phenomenon should disappear. I wonder if you compared two leathers, one with two or three times as much coating as another?

MR. GALLAGHER: We have tested all types; for example, a glazed kid will have very little adhesion, while a heavily finished upholstery leather will have a high adhesion.

DR. SHAW: Those are, of course, different types of leather.

The other question I had was: When you run this test and find that you are actually pulling fiber along with the film, what do you conclude on the adhesion of the finish to the leather?

MR. GALLAGHER: We simply record that a tear into the leather was obtained, and these readings are eliminated in averaging values.

DR. SHAW: This would be super-adhesion?

MR. GALLAGHER: Yes—when it goes into the grain or the grain surface.

A. SALAMATOV (Barrett & Co., Inc.): All these tests have been done on a flat leather before it was subjected to any flexing or any dynamic stretching. Now if the same test were to be repeated on the flexed leather, would the results be the same?

MR. GALLAGHER: I don't know. I would say yes.

MR. SALAMATOV: Out of past experience we know that a static test does not mean very much and only the dynamic test really brings out the value of a certain procedure. Would this be the same with the nitrocellulose finishes for upholstery leather?

MR. GALLAGHER: We can imagine that upon flexing, if the bond between the finish film and the leather were weakened, the difference would be shown up in this test.

DR. BORIS MONSAROFF (Hamilton, Ontario, Canada): It seems to me that if you apply an adhesive to a finish, you may have a chance of forming a new film containing the adhesive and the material which is in the finish; then you are getting a film of quite different characteristics from the original. So I doubt personally whether it is a fair test.

You may run into plasticizers, used with the resins in finishes, which combine with the adhesive. What you are testing there is not the original film but the film which you have formed by a combination of the adhesive and the film present.

And referring to a remark of Mr. Salamatov—I think he is quite right that in a porous or flexible material the flexing has an effect on the adhesive, too. I had that experience in textiles as well as in leather.

MR. GALLAGHER: That may be ture, but we are using very thin adhesive film thicknesses. I think the Scotch-Weld ranges two to four mils in thickness. Actually, under the temperatures of preparing the specimen, very little fusion or movement of the binding film is noted.

DR. MONSAROFF: It is worth investigating. It depends on the character of the film. As far as the character of the film is concerned, it also is very thin. Sometimes they apply films that are much less than a mil.

JOHN H. PORTER (Prime Leather Finishes Co.): What variances and results have you found due to the number of finish coats applied to the leather, also to the age of the finish on the samples tested?

MR. GALLAGHER: In general, I think that the base coat is the coat that is going to determine the finish adhesion. We have run a number of tests on leathers without top coats—that is, experimental finishes. They compare quite favorably with, or are in the same range as, finishes that are top-coated. Adhesion is going to depend on the adhesion of the first coat.

DR. ROBERT STUBBINGS (Lehigh University): In this discussion Mr. Gallagher said that in cases of samples where the leather was torn from the grain along with the finish, they just eliminated these samples from consideration. It would seem to me that any finish which is capable of pulling the leather apart would have to be rated at the highest end in the rating test,

and if you discard samples of this type, you are actually ruling out materials which have shown tremendous adhesion. I would think there would have to be some way of taking care of that.

MR. GALLAGHER: That is very true. I did not mean to imply that we eliminated from further consideration, for example, the resin we are investigating. Quite a bit of doubt exists in those figures in that you are actually removing leather and that on different specimens the amount of leather removed would vary. We do record our values with the notation that tearing into the leather occurred. We are quite happy when that happens on a finishing system.*

DR. STUBBINGS: It would seem to me that the deeper a finish penetrates into a leather, the harder it should be to remove it and the more leather it should take with it. I wonder if there is any part of this test which includes a measure of the amount of grain that is stripped as a measure of the penetration of the finish into the original leather?

MR. GALLAGHER: No. We have not taken that into consideration.

DR. SHAW: I would like to add to what Mr. Salamatov said that I think the relation between flexing and degree of adhesion is very important. In most of our own work on examining adhesion, admittedly we do not measure it, but we can see very clearly the difference between something which has good adhesion, fair adhesion, or bad adhesion, by simply flexing the leather sufficiently long and then looking at the cracks under a magnifying glass, or a binocular microscope. It is important to remember—and this is where poor adhesion will show up in actual practice—flexing of the leather.

*Table III shows how such data may be handled. In this case the treatments were ranked according to the number of samples in which tearing of the leather occurred. Then a rank correlation method was used to show a high degree of correlation between the two sets of results.

Only one tanner is mentioned in the Bible—the Simon who was, in all probability, a member of the church at Joppa, and in whose house Peter found a temporary home when the messengers of Cornelius were informed: "He lodgeth with one Simon, a tanner, whose house is by the seaside." There are numerous wells of water in close proximity to the town of Joppa. This would render it a suitable locality for a tannery, and the adjacent port would facilitate the shipments of a cargo in great request, not only through all the Mediterranean coast, but far up the Nile, and among the semi-civilized dwellers of Northern Europe. Several tanneries of great antiquity still exist near the shore, one of which is said by tradition to have been that of Simon, the tanner.

—*Leather Manufacture*. John W. Stevens. Chicago: The Shoe and Leather Review, 1890.

LIFE LINES

Brief Biographies of Our Contributors

Dr. Rubin Borasky is a Senior Scientist in the Biology Operation, Hanford Laboratories, of the General Electric Company, Richland, Washington. Prior to his association with General Electric, Dr. Borasky was a member of the Hides, Tanning Materials, and Leather Division, United States Department of Agriculture, where he conducted research on the fundamental chemical and physical properties of collagen. "Collagen Reactivity with Metals" is his eighth publication on the subject. His current interest is the deposition and metabolism of radioactive metals in skeletal tissue. Dr. Borasky received his A.B. and A.M. degrees from Temple University and his Ph.D. degree from Georgetown University. In addition to being a member of the American Leather Chemists Association, he is a member of the American Chemical Society, Electron Microscope Society of America, cofounder and honorary member of the Philadelphia Electron Microscope Society, honorary member of Alpha Sigma Pi (Biology Honorary Society of Temple University) and cofounder and current president of the Mid Columbia Science Foundation. This organization is devoted to increasing youth interest in scientific professions and improving science teaching in public schools.

Sverre Dahl—See the April, 1957, *Journal.*

Nicholas D. Gallagher—See the September, 1956, *Journal.*

Maynard B. Neher—See the September, 1956, *Journal.*

Victor G. Vely received his M.S. degree from the University of Pennsylvania in 1953 after completing undergraduate work at Wittenberg College, Springfield, Ohio. He was engaged in biochemical research for two years while serving in the U. S. Army. He has been associated with the leather technology group at Battelle Institute since March, 1956.

Like many other useful arts, and this is particularly true of those arts which rest on a basis of chemistry, the knowledge of tanning was brought from the East by the Moors. Morocco and Cordovan, names which still persist in the leather trade, are of direct Moorish origin. During the Middle Ages, the leathers of the wealthy continued either to be made in the East, or by those who had learned the methods of the East. Later, Russian and Hungarian leathers became articles of commerce, the art having spread overland north and west of Constantinople, as it had spread along the southern coast of the Mediterranean. The leathers made under the Eastern influence were principally the light leathers.

—*Lactic Acid In Leather Manufacture.* Alan A. Claflin and Harry P. Corson. Boston: The Avery Chemical Company, 1920.

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THE COVER

Courtesy of U. S. D. A. Photo by M. C. Audsley.

The cover picture is that of the Eastern Regional Research Laboratory of the United States Department of Agriculture located at Wyndmoor, Pennsylvania, a suburb of Philadelphia. The Laboratory is headquarters for the Eastern Utilization Research and Development Division of the Department's Agricultural Research Service, where utilization investigations on a number of important agricultural commodities are being carried out, including studies on hides, skins, and leather.

The Laboratory was established in 1940 as part of a national program of the Department to seek new and wider uses for agricultural commodities, particularly those in serious surplus. Although work on hides and leather had been carried on in the Department for many years prior to this, the program was transferred to the Eastern Regional Research Laboratory shortly after it was established and has continued there since that time. A staff of some 25 research workers, mostly chemists and a few bacteriologists, is assigned to this program.

Research on hides, skins, and leather includes investigations on the development of improved methods of curing, preserving, and unhairing hides to increase the value and utilization through better and more uniform grading and to reduce shipping costs; improving the quality of leather and developing newer tannages through chemical modification of the hides; preparation of purified collagen as a reference material for evaluating the changes occurring during the processing of hides; and the reaction of hide substance with tanning agents in the production of leather. Investigations are also being conducted on natural tanning materials, the improvement in serviceability and quality of vegetable-tanned leathers through retannage, and pretannage with aluminum salts and others.

ABSTRACTS

Principles of a Final Biological Purification of Tannery Effluents. V. Kubelka. *Veda Vyz. Prum. Kozedelnem*, **1**, 113–36 (1956).—Biological control of the influence of tannery effluents on the receiving stream is described. The number of microorganisms in the stream diminishes with content of organic matter. Aeration is accelerated by growth of green organisms. Streams are graded in 5 classes with respect to free O_2 content and character of life supported. Seasonal effects on self-purification are discussed. Minimum O_2 contents for survival of various fish species are given. Curves relating reaeration to temperature are given. The determination of B.O.D. and the effect of temperature on B.O.D. are discussed. B.O.D. cannot be the sole criterion for planning purification plants. Its determination in heavily contaminated waters, which require dilution, is deprecated. Conditions for good final biological purification include good preliminary sedimentation, freedom from poisons such as arsenic and sulfides, previous mutual precipitation of lime-yard and vegetable-tan-yard effluents, thorough mixing of effluents to obtain uniform chemical composition, pH value from 5 to 9 (optimum 8), and uniformity of flow throughout the 24 hr. Purification by percolating beds requires much land. Purification in ponds is theoretically ideal but requires large surfaces. The purification by the activated-sludge system requires that the tannery effluent be diluted, preferably with domestic sewage. The minimum necessary dilution is unknown. One Russian authority says 1 : 1, but probably a greater dilution is necessary. One city permitted 40% of tannery effluent but encountered frequent failures. Another authority considers 15% of tannery effluent to be the maximum. Perhaps the best method which is today economically possible is to impound well sedimented effluent in lagoons and release the contents to the rivers during flood periods. L.M.

Report on a Trip to Holland. H. Lutun. *Bull. Assoc. Franc. Chimistes Inds. Cuir.*, **18**, 211 (1956).—The report is mainly concerned with the rapid vegetable tannage of sole leather practiced in Holland. Some information is given on beamhouse practices for heavy hides and about the Research Institute. The technique of vegetable tanning is based not only on definite physical and chemical norms (density, acidity, temperature, duration) but also on different types of tanning materials used as well as on judiciously selected tanning blends. In Holland chestnut is still the principal tanning agent in preference to quebracho. Thanks to English tanning procedures adapted especially to wattle, this material is used as a dispersing agent for astringent tannins, but through acidification it becomes astringent itself and makes a very firm leather. Next to these two principal tannins, eucalyptus, Myrtan (*Redunca*), and sulfite cellulose from Norway follow in decreasing order of importance and finally a whole array of synthetic tannins used for decolorizing. Tanning methods vary through the influence of technicians from neighboring countries and through the perfection of a system developed by the Institute of Research in Wallwijk. All tanneries treat finders' and manufacturers' leathers differently. The rapid tanning procedures are classified in five groups: French, English, Dutch, "Walker House" patent process, and mixed methods. In the French system progress of pH, density of tan liquors, and temperature are about the

same as in France, but the tanning time is extended, which explains the low water solubles (11%). The hides pass through 10 suspender vats (2 days in each), pH 5 to 4, Bé. 3 to 12; 1 layaway vat (10 days for manufacturers' and 12 days for finders' leather), pH 3.9, Bé. 12; drum 2 days, pH 3.8, Bé. 14; and hot pit 7 days, 40°C., pH 3.6–3.7, Bé. 16.5–17. Generally, the bends are reserved for finders' and the bellies and shoulders for manufacturers' leather. In the English system the intensity of the tannage depends not only on the chemical affinity of tans and non-tans to the hide but also on physical effects like swelling. Further, this system makes use of the influence of organic and inorganic non-tans on the speed of penetration. Exact control of pH, liquor strength, and balance between tannins, non-tans, acids, and salts is indispensable. Finally, the dissolving of the tanning materials must be executed in such fashion that the liquors from the hot pits do not form sludge when introduced into the cold pits. These liquors are slightly bisulfited at the boiling point for 12 hr. and acidified with 80% formic acid (1.5–2% based on solid extract) to a pH near 3.3. The hides pass through 10 suspenders (1 day in each), pH 3.8–3.2, Bé. 2.7–5.3, tannin 0.5–7.2%, nontannin 2.9–2.0%, acid 22–70 meq/l, equivalent mg. H_2SO_4 per l. per day 14.5–1.0, salt 201–133 meq/l; 8 layaways (2 days in each), pH 3.4, Bé. 11–18, tannin 14–25%, nontannin 4–6%, acid 110–159 meq/l, salt 232–360 meq/l; and 4 hot pits (2 days in each), 40°C., pH 3.4–3.3, Bé. 17–18, tannin 23–26%, nontannin 6.6–7.1%, acid 158–149 meq/l, salt 342–228 meq/l. Vat 10 is strengthened daily with 1/5 liquor from layer 1 to which is added an equal volume of rinse water from the leather coming from the hot pits. Layer 8 is strengthened every other day with 2/5 liquor from hot pit 1 and 3/5 fresh extract. When coming from the suspender yard (12 days), the leather still shows a raw streak of 1/4 of its thickness. After the first layer penetration is complete. Tanning time is 40 days at the most. Tail liquors show the following characteristics: Bé. 2.2, pH 5.7, tannin 0.4%, nontannin 2.25%. With this process a leather of the following analysis is obtained calculated on degreased leather with 14% moisture: cold water solubles 16.9; warm water solubles (45°C.) 22.0; ash 0.83; hide substance 35.55; pH 3.58; degree of tannage 130; yield 77.9%. In the "Walker House" process, a patent of Walker Extract & Chemical Co., a special wattle extract is employed exclusively. After a standard beamhouse procedure the hides are rinsed by hanging for a day in cold water, followed by a two-day rocker in a liquor of "Nufern Powder" at 3° Bé. and pH 4.5. This liquor is strengthened for each new pack with the powder and the pH adjusted with formic acid. In a third vat the hides are rocked for one day in cold water to eliminate superficially the swelling agent. The swelled white hide does not change in thickness during the following tanning procedure regardless of pH, because the fibers are fixed in space. The tannage takes place in 6 vats containing liquors of high density. The leather is 80% penetrated after 24 hr. in the first vat. The leather remains 24 hr. in the first vat (5 hr. still, 19 hr. agitated), 20°C., pH 4.5, Bé. 7; 7 days each in vats 2 and 3, 20°C., pH 4.0–3.5, Bé. 14–16; and 2 days each in vats 4–6, 40°C., pH 3.1, Bé. 18. After piling down for 4 days the leather is bleached in a wattle extract containing bisulfite, at 16 Bé. and pH 4. By adjusting the acid and salt content, either a supple or a firm leather can be obtained. The Dutch System, highly recommended by the Wallwijk Institute, seems to be the best utilization of physical methods of penetration and following fixation of the tans, combined with the chemical system of English tendencies, though the acidification makes use of formic and citric acids. The process is, however,

hardly in use at present. The hides pass through 3 rockers (1 day in each), pH 3.8–3.2, Bé. 3.0–4.1, 20°C.; 8 layaways (2 days in each), pH 3.2 (adjusted with HCOOH), Bé. 10–17, 20°C.; and 4 hot pits (2 days in each), pH 3.2 (adjusted with citric acid), Bé. 17–18, 40°C. They are then bleached at 40°C. with wattle, bisulfite, and HCOOH at pH 3.7, Bé. 20, for 20 hr. The composition of the tanning blend is wattle 90%, myrobalans 5%, and ordinary quebracho 5%. Though all Dutch tanneries use systems more or less similar to those previously described, some have their own very typical methods, of which two are cited: (*a*) A lattice drum rotates at 8 revolutions per hour, half-immersed in a vat containing the tan liquor. The leather is attached to the lattice sides, and the principle of the process consists of immersing the leather half the time in the tan liquor and half the time exposing it to the air. It is claimed that fixation and oxidation balance the penetration, since the movement is very slow. The leather is pretanned in 6 vats (2 days in each), pH 3.5–3.3, Bé. 4.6–6.5, 20°C. This pretannage is followed by the drum tannage at pH 3.3, 21 days at Bé. 9–10 and 30°C. and 8 days at Bé. 15.5 and 35°C. (*b*) Some tanneries use a semichrome process. After a pretan with chrome alum (3.5% on white weight) and slight basification there follows a tan yard of 4 vats, 2.5 days in each, pH 3.3–3.2, Bé. 2–8. After this tannage the hide shows no raw streak, and after wringing, the leather is introduced into warm liquor to fill the interfiber spaces (pH 3.5; Bé. 10, 11, and 16; 35°C.; 2 vats 12 days each, 2 days in a drum).

Beamhouse practices.—Generally, the hides for rapid-tanned sole leather come from Belgium and France, but there are also Frigorificos, packers', and renderers' hides. The soak is always activated by mechanical and chemical means. Sometimes a small amount of hydrated lime is added to the soak water of salted hides. It seems that the reaction $Ca(OH)_2 + 2\ NaCl \rightleftharpoons CaCl_2 + 2\ NaOH$ takes place inside the hide resulting in a considerable speeding-up of the soak. This process gives unquestionable practical advantages, and it is recommended not to remove the salt from the hides before soaking.

The Wallwijk Research Institute.—This Institute is composed of a Leather Control Station and a Tanning School with laboratories for physical and chemical testing facilities. For the physical tests Holland has adopted the German norms. The Institute issues a Quality Label to guarantee leather standards to the trade. A tanner may use this label only if his product qualifies under surprise checks. T.D.B.

Phase Equilibrium in the Hydrothermal Shrinkage of Collagen. J. M. F. Oth, E. T. Dumitru, O. K. Spurr, Jr., and P. J. Flory. *J. Am. Chem. Soc.*, **79**, 3288–89 (1957).—The shrinkage of collagen denotes a transition between crystalline and amorphous phases. The stress required to maintain equilibrium between the phases should be related to the temperature according to an analog of the Clausius-Clapeyron equation. Fresh rat tail tendons, cross-linked with HCHO, were immersed in 3*M* KCNS and allowed to undergo partial contraction. The length was then adjusted to yield a force, measured on a strain gage, that remained constant for at least 30 min. The observed force was independent of degree of shrinkage as long as a crystalline region remained. The latent heat of fusion of collagen was calculated from the data obtained, using the equation referred to above. The results agree with those obtained by other methods and compare favorably with those obtained for other crystalline polymers. H.B.M.

Aluminum Compounds. IV. Composition of Basic Aluminum Chloride Solution by Paper Electrophoresis. H. Tanabe. *J. Pharm. Soc. Japan*, **77,** 33–36 (1957); **V. Effect of the Concentration of the Solution on the Condensation of Hydroxoaluminum Ion, and the Relation between the Condensation and the Length of Migration in Paper Electrophoresis.** *Ibid.*, 37–40; **VI. The Composition of Basic Aluminum Sulfates Prepared from Basic Aluminum Chloride Solutions of Various Compositions.** *Ibid.*, 41–45; **VII. Relationship between the Compositions of Basic Aluminum Chloride Solution and the Properties of Basic Aluminum Sulfates.** *Ibid.*, 45–50; **VIII. Determination of the Composition of Basic Aluminum Sulfates and Their Thermal Decomposition Products by Pyrolysis Curves.** *Ibid.*, 50–54; **IX. Basic Aluminum Sulfates and Their Decomposition Products by Infrared Spectroscopy.** *Ibid.*, 54–62; **X. Basic Aluminum Sulfates and Study of Their Thermal Decomposition Products by X-ray Diffraction Methods.** *Ibid.*, 63–68; *Chem. Abstr.*, **51,** 7921*d*.

Matacollagen as the Apparent Elastin. I. Banga, J. Balo, and D. Szabo. *J. Gerontol.*, **11,** 242–50 (1956); *Chem. Abstr.*, **51,** 8165*f*.

Solubilization of Rat Tail Collagen. E. T. Dumitru and R. R. Garrett. *Arch. Biochem. Biophys.*, **66,** 245–47 (1957); *Chem. Abstr.*, **51,** 8168*c*.

Preparation of Soluble Modification of Keratin. A. Berlin, E. Kirina, and L. Kuznetsova. *Myasnaya Ind. S.S.S.R.*, **27,** No. 6, 48–51 (1956); *Chem. Abstr.*, **51,** 8463*h*.

Manufacture of Picking Band Leather by the Combination of Sulfur-Oil-Vegetable Tanning Method. S. N. Bose. *Bull. Central Leather Research Inst., Madras*, **3,** 344–48 (1957).—Buffalo butts are soaked, limed 3 days with lime and Na_2S, delimed with $(NH_4)_2SO_4$, pickled 24 hr. with 2.5–3% H_2SO_4, 10–12% NaCl and 125–150% H_2O, horsed, and depickled with 15–20% $Na_2S_2O_3$ in 60–80% H_2O for 24 hr. The depickled stock is horsed 1–2 days, hung overnight, then stuffed with 10% of a 1 : 1 mixture of mutton tallow and fish oil, at 45°C. for 2 hr. The butts are hung in a hot room for 1 week, after which the stuffing process is repeated and the butts are hung for another week. The leather is then retanned with sulfited quebracho extract. H.B.M.

Research on Collagen and Its Changes during Tanning. A. L. Zaides. *Nauch. Issled. Trudy CNIKP*, **21,** 3–28 (1952).—Collagen fibrils possess well oriented crystalline regions and unoriented regions; the latter confer pliability, and the former are responsible for thermal shrinkage and oriented absorption of crystalline and amorphous regions of adjacent fibrils coincide. Subfibrils are cate regions of different densities. The fibrils are about 1000 A. wide, and crytalline and amorphous regions of adjacent fibrils coincide. Subfibrils are

formed when fibrils are treated with enzymes or acids. Treatment with $Ca(OH)_2$ or with pancreatin, as practiced in the tannery, does not change the electron microscope structure of the fibrils, but on prolonged treatment with $Ca(OH)_2$ electrovalent and H-bonds are broken, knots appear in the fibrils, and cross-striations no longer are visible. Pancreatin and dilute acid break electrovalent bonds and cause appearance of subfibrils. Tannage brings out further details in the fibril axis. The cross-striations are not changed by $(NH_4)_2SO_4$ but are destroyed by NH_4CNS. Since silk fibers show a different structure under the electron microcope, the cross-striations of collagen fibrils may be related to amino acid side chains. L.M.

The Changes in Cross-linked High Polymers by Mechanical Destruc- and Pepsin on Collagen. L. S. Shestakova. *Nauch. Trudy MTILP*, **5**, 22–31 45–51 (1955).—Mechanical destruction by milling of hide powder and other high polymers was studied. When hide powder is milled (in air?) it is relatively easy to reduce the particle size to 1–3 microns; further size reduction is more difficult, probably because the macromolecular dimensions of collagen have been reached. The size limit of 1–3 microns generally is reached on milling for 60 hr. The product forms a relatively stable dispersion in water, and the particles swell considerably. After milling for 100 hr., partial destruction of cross links appears to have taken place, and the hide powder dissolves partially, giving a solution of low viscosity. After milling for 150–170 hr. hide powder is completely soluble in water at 18°–20°C. Hair behaves similarly, and other polymers gain solubility in appropriate solvents. Milling of collagen in CCl_4 produces a coarse, unstable dispersion of short, broken fragments of fibers; the product is, however, soluble in water. Milling of hide powder in water yields gelatin. The destruction of polymers begins with the least stable links, chiefly H-bonds and salt links. Fibrous polymers are cleaved initially into thinner fibers, but on further milling, the assymetry diminishes. Milling in different liquids varies with the contact angle of wetting. Milling in nonpolar liquids proceeds much the same as in air. L.M.

Determination of Some Factors Influencing the Action of Trypsin and Pepsin on Collagen. L. S. Shestakova. *Nauch. Trudy MTILP*, **5**, 22–31 (1955).—The action of trypsin and pepsin was measured on collagen (split hide) that was either (*A*) washed for 16 hr. at 10°C. and then dehydrated with 50% and 96% ethanol, or (*B*) limed for 30 days in 1.2% $Ca(OH)_2$ solution, washed, delimed with HCl to a weakly acid reaction toward methyl orange, and dehydrated as for *A*. The tests with trypsin were done at pH 7.9–8.2 in borate or phosphate buffers; those with pepsin at pH 1.60–1.65 in HCl + KCl. All tests were run for 5 hr. at 37°C. Quantities measured were "hydrolysis" (fractioned solubilized ?) determined in the spent enzyme solution, and "solubility", the further quantity solubilized when the system was heated at 65°C. for a further 90 min. In 1% trypsin the values obtained were : *A*, hydrolysis 10.6%, solubility 3.45%; *B*, hydrolysis 57.8%, solubility 41.4%. In 1% pepsin the corresponding values for *A* were 1.1 and 8.3%, and for *B* 48.6 and 14.8%. It is alleged that trypsin and pepsin catalyze the hydrolysis of the principal bonds of the collagen chain. L.M.

Distillation Apparatus for Moisture Determination. T. Barr and J. I. Yarwood. *Chemistry and Industry*, **1957,** 803–5.—A description is given of a modified Dean-Starke apparatus that permits greater accuracy of measurement of the distilled water. H.B.M.

A Semimicro Method of Fat Extraction. P. Wix and J. W. Hopton. *Chemistry and Industry*, **1957,** 805–7.—A 24-unit extraction apparatus using petroleum ether is fabricated from 7″ x 1″ test tubes connecting to reflux condensers by standard taper joints. The sides of each test tube are indented to support a 16 x 60 mm. capsule. Heating is done in a water bath thermostatically regulated to 60°C. Each determination employs 0.2–2.0 g. of sample and 25 ml. of petroleum ether. Advantages claimed are elimination of fire risk and danger of damaging the sample if the apparatus boils dry during overnight extraction, as well as economy of solvent. H.B.M.

Standardization and Evaluation of Different Methods for the Quantitative Estimation of Protease Activity. S. M. Bose and W. Madhiva Diva. *Bull. Central Leather Research Inst., Madras*, **3,** 329–43 (1957).—The authors measured the activities of trypsin at pH 8.0–8.5, pepsin at 2.0–2.5, papain at 5.0–6.0, and "calotropain" (a protease from the latex of the maddar plant, *C. gigantica*) at 4.0–4.5, by 7 familiar methods. Anson's colorimetric method (colorimetric estimation of tyrosine liberated from egg albumin substrate) is regarded as the most convenient, sensitive, and precise. Of the other methods tried, the formol titration, Lohlein-Volhard, Fuld-Gross, gelatin viscosity, and nonprotein nitrogen methods all gave satisfactory results, but the alkali titration method of Willstatter and Waldschmidtleitz failed to give reproducible results because of end point uncertainty. Substitution of α-nitroso-β-naphthol or Millon's reagent for Anson's phenol reagent in determining liberated tyrosine was found to be disadvantageous. H.B.M.

Chrome-Vegetable-tanned Upper Leather ("Yuft") with a Higher Resistance to Water Penetration. I. I. Etingof and V. N. Semenova. *Nauch. Issled. Trudy CNIKP*, **19,** 47–69 (1951).—Addition of ozokerite, melted with paraffin before adding to the grease mixture, is said to be beneficial. L.M.

Preparation of Anthracene- and Naphthalene-Base Syntans with a Low Ash Content. P. Y. Frenkel and P. S. Konovalenko. *Nauch. Issled. Trudy CNIKP*, **19,** 16–26 (1951).—The ash content is reduced by sulfonating with 90% of oleum instead of 137% of H_2SO_4 (92–94%). L.M.

Physicochemical Methods of Analysis for the Evaluation of Raw Hides and Skins. G. I. Kutyanin. *Nauch. Issled. Trudy CNIKP*, **19,** 3–16 (1951).—Putrefaction of steerhide at 22°–25°C. and 100% relative humidity was studied by determining soluble protein, NH_3, pH value, and shrinkage temperature, and by applying the phenol-NaOCl, nitroprusside, Voisin-Ehrlich, and Millon reactions to the moist pelt or to extracts to detect decomposition products. L.M.

Syntan PL. K. H. Toporovskaya. *Nauch. Issled. Trudy CNIKP*, **24,** 18–29 (1955).—This syntan, which is used on a large scale in the USSR, has a purity of 54, and yields leather with T_s 73°–75°C., tanning value 58, and hydrothermal stability 65%. The acidity of Syntan PL is lower than Syntan AN or Tannigan Extra A. The Innes difference figure is 0.3. Syntan PL resembles oak wood extract in many of its properties. It has an antiseptic action in tan liquors. The tannin content is lowered by boiling. Tanning experiments at different pH values gave 31% combined tannin at pH 3.5–4.5 and 28% at pH 7.0. Syntan PL may be used to tan both heavy and light leathers. L.M.

Tanning by Means of Syntan PL. V. G. Suchkov. *Nauch. Issled. Trudy CNIKP*, **24,** 58–81 (1955); cf. preceding abstr.—This syntan may be used alone or in mixtures for tanning sole and russet leathers. Leathers tanned with Syntan PL alone, and retanned with Cr or Al salts, gave tanning values of 74 and 46 depending on the ratio of liquor to pelt (1 : 1 or 2 : 1). Pretannage with Cr was disadvantageous: a leather with tanning value of only 50–53 was obtained, and its water absorption was high. In tanning with Syntan PL alone, best results were obtained with pickled pelt. Retanning with 6% potash alum for 90 min., followed by 1% Na_2CO_3 on the pelt weight and then 2% fat for 30 min., gave a harder sole leather than retanning with Cr. The alum leather contained 1.4–1.5% Al_2O_3, and its hydrothermal stability was 89–100%. A maximum of 50% Syntan PL can be used in mixtures, and the admixed vegetable tannin must be sulfited. Retannage may be done on prechromed pelt at pH 4.5–5.0, using 24% tannin on the pelt weight. Filling by treatment with vegetable tannin in the drum is necessary. L.M.

Improvement of Tanning Properties of Sulfite Cellulose Extracts and Syntans by Means of Organic Acids. P. Y. Frenkel and A. N. Mikhailov. *Nauch. Issled. Trudy CNIKP*, **24,** 7–18 (1955).—Replacement of the mineral acidity of sulfite cellulose extracts and syntans by organic acids has a beneficial effect on the absorption of tannin by hide powder. The ratio of tannin to nontannin improves appreciably, especially in sulfite cellulose. When lightly chromed pelt is retanned by syntans or sulfite cellulose, the presence of organic acids gives a higher initial pH value, which however does not rise during tanning. Examples are cited. L.M.

A Method for the Accelerated Determination of the Basicity of the Chromium Compound in Leather. V. L. Voitsekhovskii. *Nauch. Issled. Trudy CNIKP*, **21,** 48–60 (1952).—A quick formol-ammonia titration method is proposed. A sample of 2.5–3.0 g. of ground leather is heated with 50 ml. of 0.1*N* NH_4OH at 60°C. for 1 hr. while protected from CO_2 by a reflux cooler and a NaOH trap. The liquid is filtered into a 250-ml. flask containing 20–25 ml. of 0.1*N* HCl. The leather is washed 3 times with water at 60°C., and finally at 100°C. After cooling, 15 ml. of 40% HCHO are added. The solution is made up to 250 ml., and an aliquot is titrated with 0.1*N* NaOH, using phenolphthalein. A duplicate determination is run without leather. The difference between the 2 titrations gives the acid combined with Cr in the leather. In the case of colored leathers electrometric titration is necessary. The proposed method is said to be more exact than the USSR official gravimetric method. L.M.

The Preparation of Water-soluble Leather Oiling Materials by Addition of Bisulfite to Unsaturated Oils. I. Sulfiting Codliver Oil. A. Küntzel and L. K. Schwörzer. *Das Leder*, **8**, 5–13 (1957).—If H_2SO_4 is attached to the fatty acid or the glycerin portion of an oil or fat through a -C-O-S- group, the chemical change is known as sulfating; if attached through a -C-S- bonding, the change is sulfonating. The sulfate is easily split by acid, and if a sulfated oil were used to oil chrome leather there might be a splitting of the sulfuric acid ester group and deposition of oil on the leather. The sulfonate is stable to acid. A brief review is given of methods for sulfonating organic compounds to form syntans, or wetting agents. Making emulsifiable fats by oxydative sulfonation is described in 4 I. G. Farben patents, DRP 545,264; 551,424; 672,491 and 672,492. The basic procedure was to blow air for 20–50 hr. through a mixture of 100 parts by weight of train oil and 50 parts of 40° Bé. $NaHSO_3$ solution heated to 60°–80°C. A later patent by Fabrik Stockhaüsen, DRP 721,991, is based on heating for over 25 hr. at 70°–110°C. without air or other oxidizing agent. The patents do not give a clear picture of the mechanism and are not in entire agreement, so a systematic study of the sulfiting process was undertaken. A test was conducted by treating 100 g. of oil with 50 g. of 40° Bé. bisulfite solution in a 3-neck flask in a water bath. The flask was fitted with a stirrer, a reflux condenser, and a tube through which air in fine bubbles was passed into the mixture. The progress of the reaction was tested by shaking (15 times) 5 ml. of the reaction mixture and 15 ml. of water and noting whether there was (1) a stable emulsion, (2) creaming with no separation of oil, (3) creaming with separation of oil, or (4) complete separation of oil. The reaction product was analyzed by the Panzer-Niebuer method (*JALCA*, **48**, 328) and the fractions by standard methods. The Wobourn method [*Ind. Eng. Chem., Anal. Ed.*, **13**, 782, (1941)] was found to be best and most rapid for determining "total" I_2 no. The difference between I_2 no. and thiocyanogen value, or "discrepancy", was related to sulfonation because the greater the discrepancy, the greater the tendency of the oil to react with bisulfite. The acid-stable sulfonic acid was determined by subtracting the amount of sulfur (SO_3) present as sulfate, unused sulfite, and organically bound but hydrolyzable sulfur, from the total sulfur as found by the bomb method. Analyses of the sulfited oils are given showing percentages of moisture, ash, oxidized fatty acid, alcohol-soluble and petroleum ether–soluble matter, acid number, and sulfur balance. The cod oil had the following constants: acid no. 2.7, I_2 no. 160.2, unsaponifiable 1.1, saponification no. 183.2, and thiocyanogen value 89.8. At various treatment temperatures the percentages of acid-stable sulfonic acid were as follows: 65°, 2.8%; 75°, 3.1%; 85°, 3.2%; and 95°, 3.0%. The optimum sulfiting temperature range is therefore from 75° to 85°C. Increasing the proportion of bisulfite above 2:1 did not improve yields but led to greater separation of Na_2SO_4 and $NaHSO_4$. Less bisulfate was not advisable unless the amount of air was also decreased. The current of air removed much SO_2, especially at the start of the reaction, but substitution of nitrogen for air resulted in no reaction. The effect of catalysts was tested by dissolving linoleate or resinate of Co or Pb in the oil before starting the reaction (ratio oil to metal 1000:1). Optimum sulfiting was found in 7–8 hr., but there was no better utilization of the sulfite. The only effect of the catalysts, of which Co resinate was best, was to shorten the time of the process. Because of the loss of SO_2 in a rapid air stream, it was advisable to reduce the flow of air. A homogeneous product was obtained in 1–2 hr. at 75°C. with an air flow of one bubble per second. It was also observed that the pH value decreased as the rate of

flow of air increased; pH measurements can therefore be used to control the amount of air and prevent an excess. There was no drop in pH of the emulsion with an air flow of one bubble per 3–4 seconds. Water is necessary for the reaction because bisulfite powder does not react with water-free cod oil; however, at the end of the process essentially all of the water must be removed. Without the reflux condenser the product was poor, and the amount of oxidized and free fatty acid was high. A clear, water-soluble oil was obtained by heating (75°C.) for 6 hr. under reflux, then 4 hr. without refluxing, to remove excess water. Addition of 5% of sulfonated cod oil to the oil-bisulfite mixture at the start of the reaction, to form a stable emulsion, shortened the time required for the reaction and reduced undesirable side reactions, such as oxidation of bisulfite to sulfate and saponification and oxidation of fat. Saponification of the fat is undesirable; sulfited fatty acid would not form stable emulsions. A closed vessel is not needed for the reaction. A good product was obtained in an open vessel covered with a lead lid with openings for thermometer, stirrer, air tube, and addition of water. During the first 3 hr. 10% of water was added to replace that lost by evaporation, after which the reaction was completed in 6–8 hr. without addition of water. I.D.C.

Progress Report on the Action of Nitrous Acid on Collagen. A. Küntzel. (Dedicated to O. Gerngross on his 75th birthday.) *Das Leder*, **8**, 34–8 (1957).—Deamination of collagen and action of HNO_2 on amino acids are reviewed. Decreased swelling in acid of deaminized collagen has been cited as evidence that HNO_2 tans, but although leather does not swell, lack of swelling is not proof of tannage. The deaminized collagen does not show restricted swelling in alkali. Nitrite-treated skin will dry to a leather-like product, but if thoroughly washed after the nitrite treatment, it will dry hard and horny. Pretreatment of skin with nitrite before Cr tanning results in a softer, more leathery product, but the same effect can be obtained with nitrite in the pickle. Nitrite will mask Cr salts and increase the basicity of the solution, but the nitrito complex decomposes after some time, releasing HNO_2 and forming a high basicity, unstable Cr compound. Softer leather is formed because nitrous gases mechanically open the fibers. Pretreating skins with nitrite before Cr tanning was of no practical value because of bad drawn grain; however the process might be useful for chamois or chrome splits. I.D.C.

Determination of the Constitution of Sulfitochrome Complexes. H. Erdmann. *Das Leder*, **7**, 198–206 (1956). **Discussion and Review of the Present Status of Our Knowledge of Sulfite-masked Chrome Liquors.** A. Küntzel and H. Erdmann. *Ibid.*, **206–8**, (1956).—Sulfitochrome complexes can arise from (1) preparation of one-bath chrome liquors by reduction with SO_2 or Na_2S_2OS, (2) masking by addition of Na_2SO_3 to chromic salt solutions, (3) neutralization of acid chrome leather with Na_2SO_3, or (4) use of $Na_2S_2O_3$ in the above processes, and also the two-bath tannage, whereby thiosulfate decomposes below pH 3 into sulfur and sulfite or bisulfite. The number of acid radicals in the Cr complex was determined by the method of Küntzel, Erdmann, and Spahrkäs (*JALCA*, **47**, 500) by titration with HCl. This conductometric method is possible because the acid liberated from the masking salt is very weakly dissociated. Only sulfite can be titrated, not the acid salt, because the second dissociation step is too weak. The number of sulfito groups in the com-

plex cannot therfore be estimated. When twice the number of equivalents of sulfite were added to a hexaquochromium salt solution, reaction according to the following equation was expected:

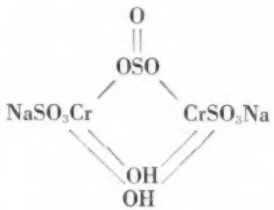
$$Cr_2(SO_4)_3 + 6Na_2SO_3 + 6H_2O \longrightarrow 2Cr(OH)_3 + 6NaHSO_3 + 3Na_2SO_4$$

(Instead of insoluble $Cr(OH)_3$ a soluble sulfito complex would form.)
This reaction did not occur because one mol of sulfite could be titrated with acid, indicating that the reaction was as follows:

$$Cr_2(SO_4)_3 + 6Na_2SO_3 + 6H_2O \longrightarrow 2Cr(OH)_3 + Na_2SO_3 + H_2SO_3 + 4NaHSO_3 + 3Na_2SO_4$$

The sulfite ion (from H_2SO_3) is bound as a bridge between two Cr atoms. If less than 6 equivalents of Na_2SO_3 per Cr were added, Na_2SO_3 could not be detected by titration. Conductometric titration with NaOH solution is based on neutralization of the acid formed by hydrolysis and that bound to Cr. For titration of a Cr salt solution with no complex-active acid anions, 3 equivalents of NaOH per Cr will be required. Addition of a complex-inactive neutral salt will increase conductivity but not the amount of NaOH required. This will also be true for a weak masking salt that is completely liberated from the complex during the titration, but a firmly bound acid radical in the complex will reduce the amount of NaOH required. On addition of sulfite to a Cr salt solution, there was a decrease in amount of hydrolyzed acid until, with 4 equivalents of Na_2SO_3 or more per Cr, no free acid was present even after aging 2 days. Addition of increasing amounts of sulfite up to 5 equivalents per Cr decreased the amount of NaOH required for titration, but more than 5 equivalents had no further effect. The effect was continuous, not stepwise, as there was a gradual increase in amount of masked, and decrease in amount of unmasked, chrome. The amount of precipitate that formed on titration decreased as the amount of sulfite increased until none was found with 4 equivalents Na_2SO_3 per Cr, although on long standing there was precipitation. When the sulfitochrome-complex solutions, containing from 0 to 8 equivalents of Na_2SO_3 per Cr, were treated with a few drops of 30% peroxide, then titrated with NaOH, the end point of the acid neutralization curve was at 2 mols of bisulfite per Cr. Of the 4 mols of bisulfite per Cr titratable with NaOH before oxidation (see equation above) only 2 were oxidized; 2 were attached to Cr and were not oxidized to sulfate by H_2O_2 but were released and titrated with NaOH. These results indicate formation of a complex containing 2 Cr atoms joined by 3 bonds (one sulfito and 2 hydroxo) according to the following equation:

$$Cr_2(SO_4)_3 + 6Na_2SO_3 + 6H_2O \longrightarrow 2NaHSO_3 + Na_2SO_3 + 3Na_2SO_4 + 4H_2O +$$



The complex is the sodium salt of a basic chromesulfito acid. This complex is similar to the sulfate complex (*JALCA*, **47,** 798), however the solution of the sodium salt of the sulfitochromic acid, if more than 5 equivalents of sulfite are present, is homogeneous, while the sulfatochromic acid is in equlibrium with a basic complex and with the hexaquochromic ion. Sulfato groups can be titrated conductometrically wth NaOH, but sulfito groups cannot. Basic chromium chloride or sulfate solutions made 1/3 basic cold gave a precipitate on addition of Na_2SO_3. If the basic solutions were boiled, then cooled, addition of sulfite caused formation of a precipitate in the chloride but not in the sulfate solutions; in the latter most of the chrome was in sulfatochrome complex. If the sulfite was added first to the hexaquochromium salt solutions, which then were made 1/3 basic, no precipitate formed in either chloride or sulfate solutions if more than 4 equivalents of Na_2SO_3/Cr had been added. Titration curves with NaOH of basic solutions were similar to those of neutral salt solutions if more than 4 equivalents of Na_2SO_3/Cr were present. The results indicate the formation of double complexes containing 4 Cr atoms. These form when two 2-Cr complexes are united by 2 OH bonds joining a Cr atom from each complex after removal of the singly bonded SO_3Na group. This constitution is based on the following facts: (1) As basicity increases, the green complex color or the sulfitochrome complex increases continually, although from doubling step to doubling step more and more sulfito groups leave the complex; therefore the observed deepening of color can only come from an increase in particle size (increase in basicity). (2) Behavior during conductometric titration with HCl or NaOH indicates that the condensation mechanism is the same at basicities from 33 to 50% as at 0–33% basicity. (3) Measurement of the absolute conductivity, found by subtracting conductivity of neutral salts from the total conductivity, shows that the conductivitv curve for the sulfitochrome complex shortens from step to step in proportion to the doubling. (4) Curves for relation of particle size and basicity of sulfito complexes agree completely with those found by Riess and Barth (*Collegium*, **778,** 62 [1935]) from dialysis and diffusion measurements in chromium sulfate solutions of increasing basicity. In the discussion the question arose as to the application of this new information on the constitution of basic sulfitochrome complexes to the well known special tanning properties of sulfite-masked chrome liquors. This work is not applicable to commercial liquors because these solutions were not aged to equilibrium, oxidation by air of sulfite to sulfate was not accounted for, and commercial liquors are more concentrated and contain sulfato and carbonato groups before sulfite is added; however, a brief review was prepared of the tanning behavior of sulfitochrome tan liquors. I.D.C.

The Influence of Water Content of Hides and Removal of Their Soluble Proteins during Soaking on the Yield and Physicochemical Properties of Tanned Leather. I. M. Lechitskii. *Nauch. Trudy MTILP*, **4,** 53–60 (1954).—The principal effects of soaking are water absorption by, and splitting of, the collagen fibers, thus increasing their internal surface. Best removal of soluble proteins was obtained by use of salts, by imparting a slight swelling, and by pickling. Tanning value and yield increase in direct proportion to removal of soluble proteins. Best results were attained by soaking in a solution containing 0.2–0.3% of Na_2Sx; this soak also gave the best tear resistance and elongation at break. Soaking in saturated $Ca(OH)_2$ solution gave bad

results; therefore the practice of liming without preliminary soaking is condemned. L.M.

The Isoelectric Point of Collagen. G. A. Arbusov. *Nauch. Trudy MTILP*, **4**, 70–72 (1954).—Changes in pH of acid and basic solutions containing collagen (hide powder) were studied. pH values were determined for solutions containing 2 g. collagen and 0.5 to 10 ml. of 0.1*N* HCl, H_2SO_4, H_3PO_4, acetic, oxalic, and citric acids in 100 ml. For inorganic acids the isoionic point was found to be pH 4.7; for organic acids the isoionic point was pH 5.7. The difference is explained by specific interactions of organic acids with collagen. The isoionic point does not always coincide with the isoelectric point. L.M.

Heat- and Sweat-resistant Insole Leather. G. Vágó and K. Fekete. *Das Leder*, **8**, 137–43 (1957).—Deterioration of the insoles is one of the most important causes of discarding shoes. Numerous types of retannages have been proposed to lengthen insole life, especially retannage with alum, chrome, or formaldehyde. Rubber soles are vulcanized onto shoes in a hot press for 3–6 minutes. Temperatures within a shoe in a press at 165°–170°C. for 11 minutes were as follows: middle of instep, 116°; toe, 120°; outer edge at ball, 128°; and inside edge at ball, 138°C. At the last location the temperature was 113°C. in 3 minutes. Such temperatures will ruin leather containing over 5% moisture. From the economic viewpoint the preferable retannage would increase weight yield or cutting value enough to pay for materials and labor used in retanning. Retanning decreases soluble matter, but this is not the entire cause of the increase in shrinkage temperature (Ts); cation-active resins which precipitate tannin raise Ts only a few degrees. For increasing the resistance of leather to moist heat, retannage with alum was best for leather tanned with hydrolyzable tannins, but HCHO was best for that tanned with condensed tannin. For example, Ts values for vegetable leather (1) before retanning, (2) after retanning with alum, and (3) after retanning with HCHO were as follows: sulfited quebracho-tanned leather 88°, 96°, and over 100°C.; chestnut-tanned leather 82°, over 100°, and 88°C. The idea of Theis that HCHO retannage raises Ts because it condenses with the tannin and increases molecular size leads to the conclusion that retannage may change semitannins to true tannins. Treatment of skin with such tannin precursors as resorcin, pyrocatechol, pyrogallol, or gallic acid changed Ts very little, but after retanning with alum or HCHO, Ts was appreciably higher. Retannage of 7 syntan leathers with alum, HCHO, urotropin, Bastanol, Kolorfix (a dicyandiamid condensate) or zinc sulfate not only raised Ts but improved the appearance of the leather and gave it more the character of straight vegetable leather. Retannage also affords some protection against sweat, has some fungistatic action, and increases both area stability and life in wear tests. Many processes and masking salts were tested; the best process from the viewpoint of cost and technical difficulties was an alum formaldehyde combination retannage as follows: Tan the soaked leather for 2 days in a vat (paddle or drum may be used) with 4% HCHO and 3% sodium bicarbonate on leather basis. Smoother leather is produced if the liquor is warmed to 30°C. Liquor can be reused 4 or 5 times if strengthened and adjusted to pH 7. Then tan in a drum with 10% alum and about 1.5% soda or the equivalent amount of

sodium sulfite or thiosulfate. Retannage can also be a dry impregnation in which only 8–12% (leather basis) of water is used to dissolve the alum. The best retannage as regards heat and sweat resistance was chrome pretannage, vegetable main tannage and alum retannage. The disadvantages of alum retannages are as follows: (1) The leather color is greenish (this can be improved by adding a little orange dye to the bath); (2) ash is very high, and the leather should be throughly washed; (3) the leather is somewhat softer and more flexible; (4) alum and chrome have greater affinity for vegetable leather than for raw hide, so there is danger of drawn grain and the retan liquor should be added slowly and warm; (5) too heavy retannage will produce leather with poor tear resistance. Hydrothermal stability may be tested by heating a specimen at 65° for 2 days in a water vapor–saturated atmosphere, then measuring tear strength. In the "box shrinkage" test the specimen is put in water for 0.5 hours, in a water vapor–saturated vessel for 3 hours (the leather then should contain 58–62% water), then heated in the box in a bath at 98°C., and examined occasionally for appearance, shrinkage, and brittleness. A vulcanizing test is conducted by putting an air-dry leather specimen, 126 mm. in diameter, against a rubber disk of the same size and 5 mm. thick, then putting the pair in a hot press for 20 minutes with steam at 3.5 atmospheres (139°C.) acting on the rubber. Ordinary leather will gelatinize in this test, but retan leather should be practically unchanged and should not shrink in area. Sweat resistance was tested by the method of Grassmann and Stadler (*JALCA*, **49**, 528) but the time was shortened from 15 days to 3 by more frequent cycling. The dry leather may be saturated with sweat solution then heated at 65° for 3–6 hours and examined. By all tests the HCHO-alum retannage increased resistance to sweat and to a greater degree than post-treatment with nontanning resins. I.D.C.

Inorganic Chemistry of Liming Chemicals. R. Appel. *Das Leder*, **8**, 1–4 (1957).—The swelling action of lime liquors depends on the pH value of the solution and is modified by neutral salts. Calcium hydroxide has a solubility of 1.2 g. CaO per 1. or 2.2×10^{-2} mols per 1., from which the pH value of a saturated solution can be calculated to be 12.64. The solubility product of lime is $[Ca] \times [OH]^{-2} = 4.25 \times 10^{-5}$, therefore addition of either Ca or OH in concentrations greater than 10^{-2} will decrease its solubility. A salt without a common ion, such as NaCl, will increase the ion strength of the solution, decrease the activity coefficient, and therefore will increase the solubility of the $Ca(OH)_2$. NaCl increases the solubility by 25–30% and polyvalent ions 2 or 3 times. The calculated pH value or 0.1 *M* NaHS was 9.9 and of Na_2S, 12.95. A graphical method is described for determining ion concentrations and pH values in the H_2S system. I.D.C.

Mechanical Removal of Pigskin Croupons. F. Stather. *Das Leder*, **8**, 63–64 (1957).—After the animal has been slaughtered, bled, and carefully washed, it is hung on a special carriage in such a position that the belly and hoofs are immersed in water at 70°–75°C.; then the bristles are removed from these parts. The animal is put horizontally on a carriage, and the croupon is outlined by cuts through the skin perpendicular to the backbone line, a hand width behind the ears, in front of the tail, and along the belly. The skin along one belly edge is loosened and clamped onto a roll which is turned by motor

and pulls the skin off in about 5 seconds. Bits of carcass are pulled off, so it is necessary to flesh the croupons by hand or machine. In another type of machine, after the croupon is outlined as above, the carcass is suspended by the hind legs, and the head is fastened in a clamp; then the neck end of the croupon is fastened in a clamp and pulled up to remove the croupon. I.D.C.

The Influence of Vegetable Tanning on the Real Specific Weight of Leather. O. V. Matveeva and A. N. Mikhailov. *Nauch. Issled. Trudy CNIKP*, **19,** 26–47 (1951).—The real density (d.) of vegetable-tanned leather was studied by the pycnometer method, using kerosene. Determinations of d. were also made on gelatin-tannin precipitates, mostly obtained with oak wood extract. The d. of pelt is 1.42, and that of oak wood tannin is variously reported as 1.60–1.64. The d. of vegetable leather is higher than the additive d. of collagen and tannin. Density increases with time of tannin and especially after oxidation on drying. Density also is increased by any pretanning treatment that increases the internal surface of the pelt, such as prolonged liming, acid swelling, or prechroming. Retanning with Cr, on the other hand, decreases d. Values obtained for d. of leather tanned with oak wood extract at 28°, 36°, and 75°C. (pretanned with HCHO in the latter case) were 1.52, 1.58, and 1.70; of leathers tanned at pH 4 for 20 days, 4 mo., 6 mo., and 10 mo. were 1.52, 1.69, 1.68, and 1.72; of tanned pelt limed the normal time, 4 days longer, and 20 days longer, then tanned 20 days, were 1.52, 1.59, and 1.68. Oxidation during tanning with enzymes of *A. niger* increased d. from 1.48 to 1.63; air oxidation at pH gave d. 1.60; prechroming gave d. 1.61, which increased to 1.70 after 3 days in pile. Piling and drying for 22 hr. increased d. from 1.45 to 1.69, and to 1.88 after 10 days. The d. of the dry matter of oak wood extract increased from 1.64 to 1.77 on oxidation. All the leathers of high d. were dark-colored. L.M.

The Argentine Leather Industry. S. Weyland. *Das Leder*, **8,** 123–28 (1957).—A description of the tanning industry in Argentina, its tanning processes, and the types of hides, skins, tanning materials, and tannery chemicals produced there. In 1935 there were 1094 tanneries employing 18,000 workers and producing 25 million dollars worth of leather. In 1954 corresponding values were 1819, 25,000, and 52 million, but at present the number of tanneries is about the same as in 1935. Between 20 and 25% of the 10 million hides produced annually in Argentina are tanned in that country, but very few of the 15 million sheep- and goatskins are tanned there. Much tanning machinery is used and also manufactured in Argentina because of the lack of skilled labor. No investigational work is being done. I.D.C.

New Developments in the Opaque Coating Field. II. K. Eitel. *Das Leder*, **7,** 126–33 (1956); see *JALCA*, **46,** 651 (1951).—Developments in pasting, pigment finishes, and polymeric binders during the past 5 years are reviewed. I.D.C.

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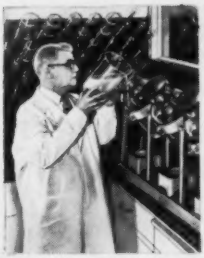

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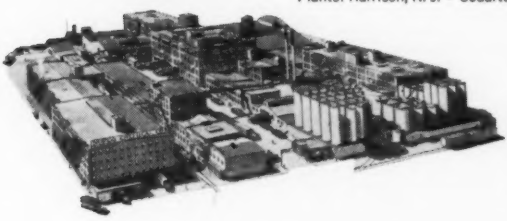

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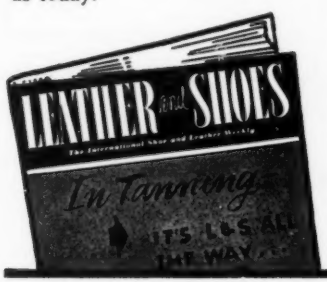

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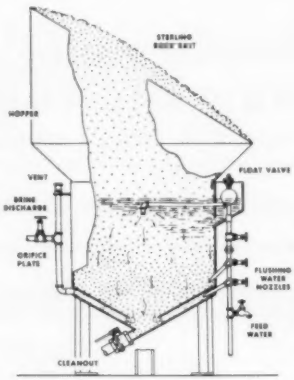

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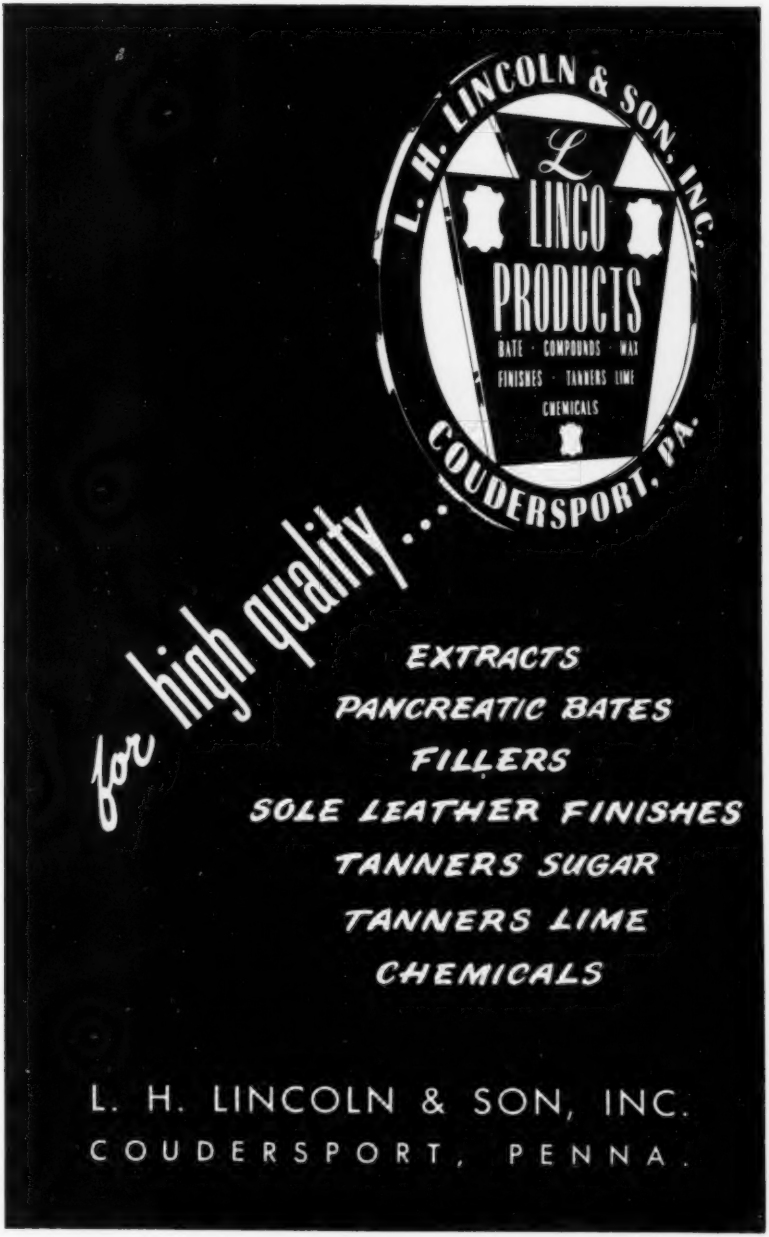
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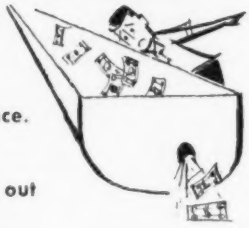

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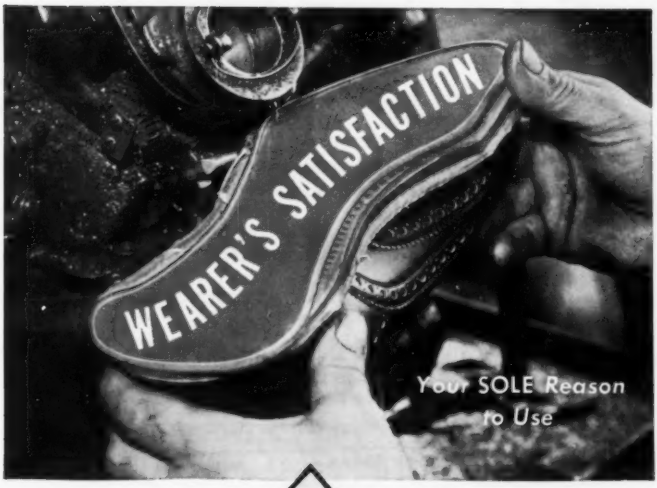

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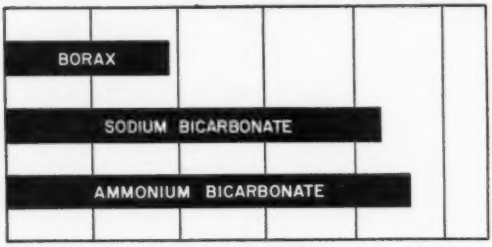
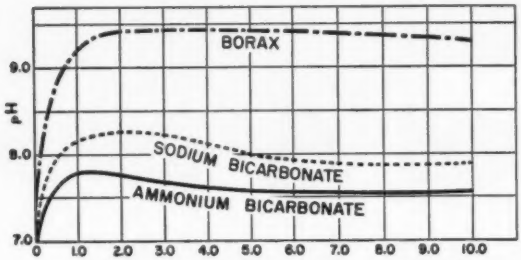


Pounds of hydrochloric acid neutralized by 1 lb. of alkali

at Lower pH for



Comparative pH of solutions at various concentrations

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